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CITRININ—PART I

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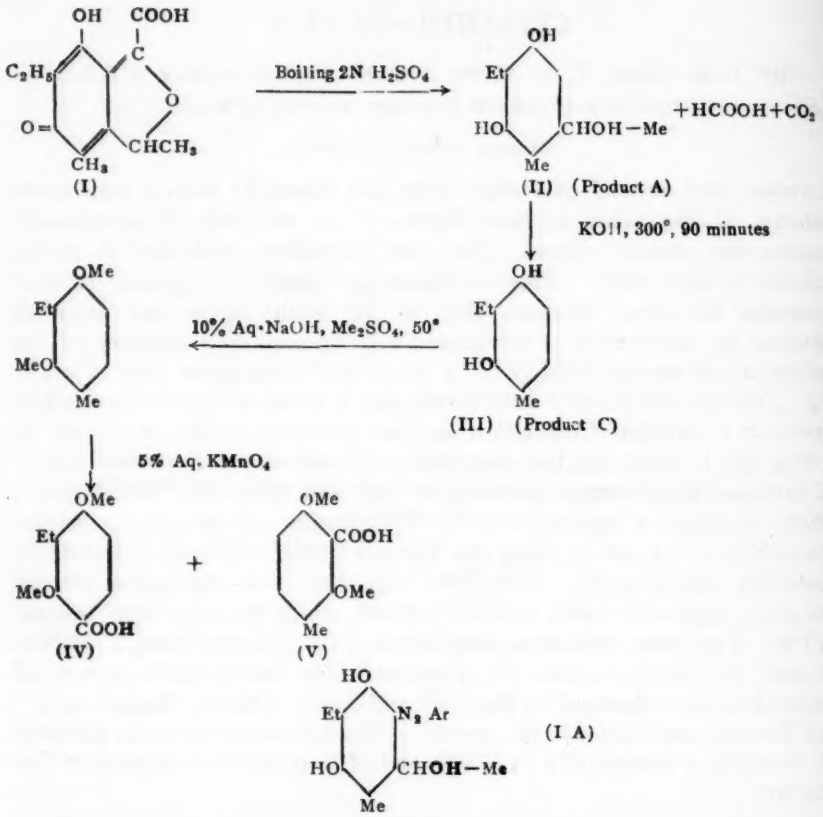
Received February 19, 1949

Citrinin, first isolated by Hetherington and Raistrick[1] from a metabolism solution of *Penicillium citrinum* Thom., is an antibiotic of considerable interest for several reasons. The pure crystalline substance is readily isolable in high yield. From a culture in Czapek-Dox glucose solution incubated for about fourteen days at 28° Hetherington and Raistrick obtained by acidification of the filtered solution and crystallization of the precipitate an average yield of 0·7 g. per l. and a maximum yield of nearly 2 g. Timonin and Rouatt[2] have shown that a strain of *Aspergillus candidus* grown in a modified Czapek-Dox medium produces citrinin in a yield of 3·86 g. per l. under the best conditions. Considering citrinin as "worthy of extended experimental and clinical trial and large-scale production", Wyllie[3] developed a method for its rapid production and was able to increase the yield to 5·5 g. per l., using the Timonin strain cultivated in a medium containing maple syrup. *Penicillium expansum*[4] and *Aspergillus terreus*[5] are other organisms which produce citrinin, which has also been isolated in 1 to 1·2 per cent. yield from dried leaves of the flowering plant, *Crotalaria crispata*, growing in tropical N. Australia.[6] The bacteriostatic activity of citrinin has been examined by Raistrick and Smith,[7] Oxford,[8] Tauber, *et al.*,[9] and Timonin and Rouatt[2]; the growth of *Staphylococcus aureus* is inhibited by citrinin in a dilution of 1 in 50,000, and of *B. subtilis* in a dilution of 1 in 2,00,000.

Citrinin crystallizes from alcohol in bright, golden yellow needles, m.p. 171·5° (decomp.), and is optically active; $[\alpha]_{\text{Hg green}}$ = about − 42° in alcoholic solution.[1] The constitution (I) was assigned to citrinin by Coyne, Raistrick and Robinson[10] on the basis of its properties and the degradation outlined in Chart I. The product (II) (Product A; colourless plates, m.p. 128–30°) was optically active, and was accompanied by an optically inactive substance (Product B; colourless prisms, m.p. 169–70°) which was considered to be a stereoisomer of Product A. Alkali fusion of Product A gave a phenol (Product C) formulated as 4-methyl-2-ethyl-resorcinol (III), the orientation of the alkyl groups in this phenol being fundamental to the proof of the constitution of citrinin. Permanganate oxidation of the dimethyl ether of Product C gave two carboxylic acids formulated as (IV) and (V).

CHART I



Our interest in citrinin began with the observation that the " therapeutic drug called Notalin " prepared by Manohar[11] was citrinin; and in view of a study[12] then in progress in this laboratory on certain aspects of the coupling of phenols with diazonium salts, which will form the subject of a later communication, the behaviour of citrinin, a phenol carboxylic acid, towards diazonium salts was examined.[13] Citrinin coupled rapidly with diazotized aniline, *o*-chloroaniline, 2: 5-dichloroaniline and sulphanilamide, yielding monoazo dyes, the nitrogen, chlorine and sulphur content of which indicated no replacement of a group in the citrinin molecule. In each case the azo dye contained a carboxyl group, and a notable property of the benzeneazocitrinins was their stability to boiling dilute sulphuric acid which degrades citrinin as shown in Chart I. These facts ruled out structure (I)

for citrinin; if (I) coupled at all with diazonium salts it could only form the neutral dyes (I A) with considerably higher values for nitrogen, chlorine and sulphur than those obtained. Further the monoazo dye containing a carboxyl group was not the sole product of the action of a diazonium salt on citrinin, but was accompanied by varying amounts of monoazo and disazo compounds which were not carboxylic acids. It was therefore clear that a breakdown of the citrinin molecule by means of a diazonium salt had to be taken into account.

Azo dyes from Product A and the phenol (C) were next examined. Both readily yielded disazo dyes, so that the structures (II) and (III) respectively assigned to them, on which the constitution (I) for citrinin depended,[10] were rendered untenable. A nuclear alkyl group in a phenol cannot be displaced during coupling with a diazonium salt, while halogen, aldehyde, acetyl and carboxyl groups can undergo such replacement under suitable conditions. Sprenger and Ruoff[15] have since shown that the melting points of Hetherington and Raistrick's acids did not correspond with those of 2: 4-dimethoxy-3-ethylbenzoic acid (IV) and 2: 6-dimethoxy-3-methyl-benzoic acid (V) synthesized by them.

Product C is undoubtedly a methyl ethyl resorcinol, as indicated by its properties, its failure to give a trisazo dye, and the fact that the disazo dyes cannot be acetylated. We have found in the course of other work[14] that azophenols in which all the positions of the phenol nucleus are occupied do not yield acetyl derivatives; but an azophenol, such as 2: 4: 6-*tris*-benzeneazoresorcinol or 3: 5-*bis*benzeneazoresacetophenone, which has an unsubstituted position, can be acetylated, although the two hydroxyl groups are sandwiched between substituents. A propylresorcinol was thus excluded. Among the seven methyl ethyl resorcinols, the 2: 4- and 4: 6-dialkyl compounds were ruled out by the ability of Product C to form disazo dyes. We then attempted to decide if (C) carried an alkyl substituent in the 2-position. A series of 2: 4- and 4: 6-*bis*benzeneazoresorcinols were prepared by coupling diazotized aniline with appropriate resorcinol derivatives, such as resacetophenone and 5-methyl-4-ethylresorcinol which could only give the 2: 4-disazo compounds, and 2-acetylresorcinol and 2-ethylresorcinol which could only give the 4: 6-disazo compounds. Absorption spectra, as well as colour reactions, distinguished clearly between the two series. Comparison of the absorption spectra (Fig. 1) and the colour reactions of the *bis*benzeneazo derivative of (C) with 2: 4- and 4: 6-*bis*benzeneazo-resorcinol, 2: 4-*bis*benzeneazo-5-methyl-6-ethylresorcinol and 4: 6-*bis*benzeneazo-2-ethylresorcinol conclusively showed that (C) was 5-methyl-4-ethyl-resorcinol (VI) or 4-methyl-5-ethylresorcinol (VII). The absorption curves

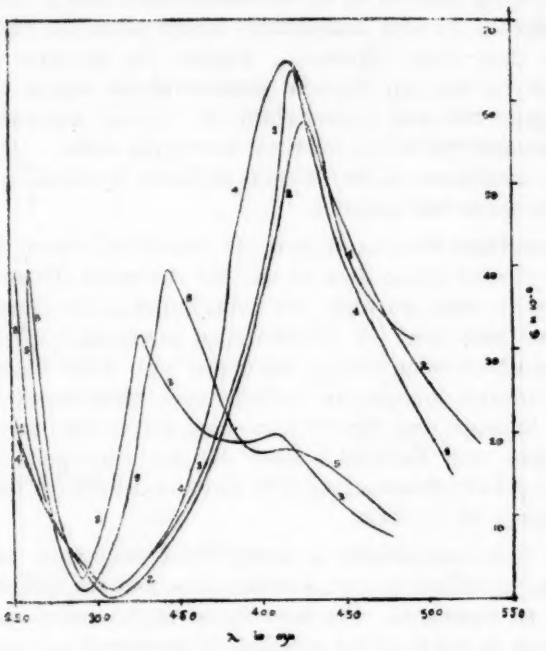


FIG. 1

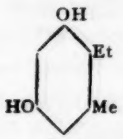
(1) *Bis*benzeneazo derivative of Product (C);
(2) 2: 4-*Bis*benzeneazoresorcinol;
(3) 4: 6-*Bis*benzeneazoresorcinol;
(4) 2: 4-*Bis*benzeneazo-5-methyl-6-ethylresorcinol;
(5) 4: 6-*Bis*benzeneazo-2-ethylresorcinol;
Solvent—Cellosolve.

for 2: 4-*bis*benzeneazoresorcinol, 2: 6-*bis*benzeneazo-5-methyl-4-ethylresorcinol and the *bis*benzeneazo derivative of (C) had a well-defined, high intensity band in the visible region ($\lambda_{max.} \sim 415\ m\mu$; $\epsilon_{max.} \sim 60{,}000$). 4: 6-*bis*-Benzeneazoresorcinol and 4: 6-*bis*benzeneazo-2-ethylresorcinol exhibited a band of relatively low intensity in the visible region ($\lambda_{max.} \sim 415\ m\mu$; $\epsilon_{max.} \sim 20{,}000$) and absorption maxima in the near ultraviolet ($\lambda_{max.} \sim 340\ m\mu$; $\epsilon_{max.}$ 36,000).

Fusing product (A) with potassium hydroxide as described by Hetherington and Raistrick, the phenol (C) crystallized from benzene in long colourless needles, m.p. 68–69°. The substance lost one molecule of water on heating and then melted at 98–99° (Hetherington and Raistrick 97–99°). Robinson and Shah[16] have mentioned that an old sample of the product,

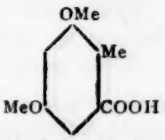
which had apparently deteriorated, melted at 65–70°; while synthetic 4-methyl-2-ethylresorcinol melted at 98–99°.

Shah and Robinson's synthesis[16] of (VI) was repeated, and it was found to melt at 79–82° (Shah and Robinson, m.p. 75–80°), while (C), as a mono-



(VI)

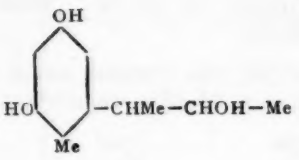
(VII)



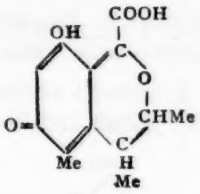
(VIII)

hydrate, melted at 68–69°, and after dehydration at 98–99°; the m.p. of (C) was considerably depressed by admixture with (VI). Cram,[17] who has synthesized (VII) and demonstrated its identity with (C) by direct comparison, has quoted us erroneously as reporting a m.p. of 65–70° for (C). The *bis*benzeneazo derivatives of (C) and (VI) melted respectively at 171° and 188°, and the mixed m.p. was lower. It followed therefore that (C) is 4-methyl-5-ethyl resorcinol (VII), although this is in conflict with the observation of Coyne, Raistrick and Robinson[10] that neither of the acids (IV) and (V) obtained by oxidation of the dimethyl ether of the phenol (C) gave the anthrachrysone reaction. We have prepared 4:6-dimethoxy-*o*-toluic acid (VIII) by the methylation of the corresponding α-resorcylic acid,[18] and found that it readily gave a bordeaux-red colour on warming with sulphuric acid (the anthrachrysone reaction); Cram[17] has recorded that the acid (VIII) synthesised by him corresponded in its properties to one of Hetherington and Raistrick's acids. The m.p. (157–58°) reported for (VIII) by Cram is in agreement with ours, while Hetherington and Raistrick's two acids melted at 142–46° and 98–99°. The failure of either of Hetherington and Raistrick's acids to give the anthrachrysone reaction may be due to their obtaining a benzoic acid only by the oxidation of the 4-methyl group.

From the formulation of (C) as (VII), it is obvious that the properties of Product A, including the formation of (VII) by alkali fusion, can only be explained by the structure 4-methyl-5-(1-methyl-2-hydroxy-) propyl-resorcinol (IX) which has been proposed by Cram. It appeared at this stage[19] that the experimental results of Hetherington and Raistrick[1] and the behaviour of citrinin towards diazonium salts would agree with the constitution (X), derived from an isochromane system. At the same time it was obvious that the coupling reaction of citrinin with diazonium salts was complex and needed to be thoroughly investigated in the light of the proposed structure (X). A complete elucidation of the constitution of the azo



(IX)

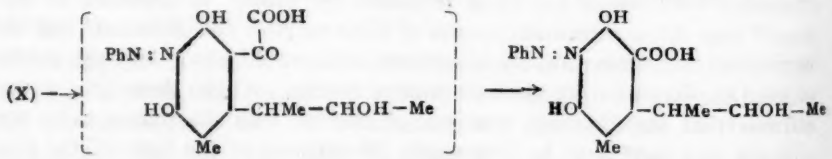


(X)

dyes obtained from citrinin and from Product A should in turn serve as a useful approach to the constitution of citrinin itself.

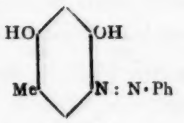
It has been mentioned earlier that the monoazo carboxylic acids obtained by coupling citrinin with various diazonium salts were much more stable to boiling dilute sulphuric acid than citrinin, and no explanation of this fact was forthcoming by assuming coupling to take place in the only vacant position without further change in the citrinin molecule (X). Carbon-hydrogen estimations immediately showed that in each case the monoazo dye containing a carboxyl group did not correspond to the monoazo derivative of (X), but to the monoazo dye (*e.g.*, XI) derived from a carboxylic acid of Product A. Thus the benzeneazo derivative, m.p. 183° (decomp.), gave the values C, 62·9; H, 6·0; N, 8·2; while (XI) requires C, 62·7; H, 5·8; N, 8·1; and the benzeneazo derivative of (X) requires C, 64·4; H, 5·1; N, 7·9 per cent. If (XI) represented the correct structure, diazonium coupling must result in hydrolytic fusion of the heterocyclic ring to form the phenylglyoxylic acid derivative (XII), followed by further hydrolysis to (XI) and formic acid. Proof that (XI) was a 2-benzeneazoresorcinol and a study of the behaviour towards diazonium salts of a 2:4-dihydroxyphenylglyoxylic acid were therefore necessary.

Coupling citrinin with diazotized aniline two neutral products could be isolated, besides the carboxylic acid provisionally postulated as (XI). One was a disazo dye, m.p. 205°, identical with the disazo dye from Product A; the m.p. and the mixed m.p. were the same, but while both gave the correct analyses for carbon and hydrogen, the disazo dye prepared from Product A gave in repeated analyses values for nitrogen about 0·8 per

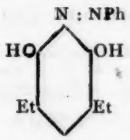


(XII) (XI)

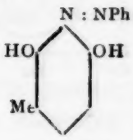
cent. higher than the theoretical requirement. The second neutral product was identical in all respects with a monoazo dye, m.p. 190°, prepared by coupling Product A with diazotized aniline. The azo carboxylic acid, assumed to be (XI), was then decarboxylated by heating it for a few minutes at its m.p. in glycerine solution, and the neutral product was found to be identical with monobenzeneazo-Product (A), m.p. 190°. Although the γ- or 2-position in 5-substituted resorcinols (*e.g.*, in orcinol and in α-resorcylic acid) has considerable reactivity in reactions such as carboxylation and the Fries rearrangement, exclusive coupling in the 2-position in a resorcinol derivative while a β- or 4-position was available seemed improbable, and the structures (X) for citrinin and (XI) for the monoazo carboxylic acid from citrinin required careful consideration by a comparison of the properties of the azo dyes with those of 2-benzeneazo- and 4-benzeneazoresorcinol derivatives. 4-Benzeneazoresorcinol, 6-benzeneazo-4-methylresorcinol (XIII), 2-benzeneazo-4 : 6-diethylresorcinol (XIV) and 2-benzeneazo-4-methylresor-



(XIII)

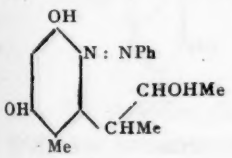


(XIV)

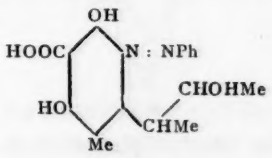


(XV)

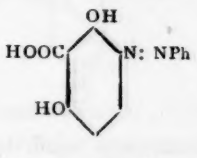
cinol (XV) were examined, and it was found that in colour and in solubility in aqueous sodium carbonate, the monoazo dye from Product A resembled the 4-benzeneazoresorcinols rather than the γ-azo compounds (XIV and XV), so that benzeneazo-Product (A) had to be formulated as (XVI) and the azo carboxylic acid from citrinin as (XVII) in preference to (XI). γ-Resorcylic acid coupled smoothly with diazotized aniline to form (XVIII). The absorption curves for (XVIII) and the azo carboxylic



(XVI)



(XVII)



(XVIII)

acid from citrinin were very similar (Fig. 2), giving further support to the structure (XVII); but confirmation by comparison with the absorption curve for the β-resorcylic acid derivative (XIX) has not been possible, since (XIX) has not yet been prepared. Coupling 4-methylresorcinol-6-carboxylic acid (XX) with diazotized aniline resulted in decarboxylation

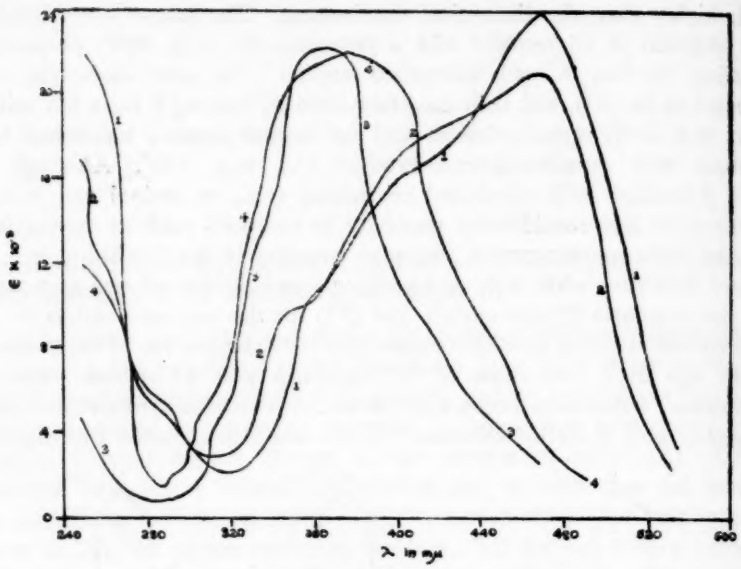
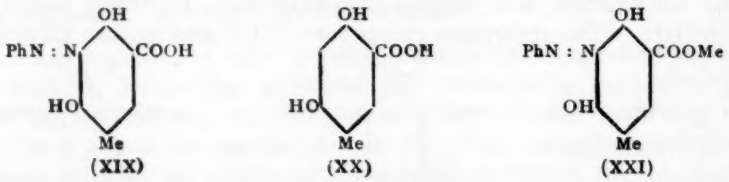


FIG. 2

(1) Monoazo dye (XI or XVII) from citrinin ;
(2) 4-Benzeneazoresorcinol-2-carboxylic acid ;
(3) 2-Benzeneazo-4 : 6-diethylresorcinol ;
(4) 4-Benzeneazoresorcinol;
Solvent—Cellosolve.

and the formation of (XIII). The methyl ester of (XX) could be coupled to form (XXI), but hydrolysis with warm alcoholic caustic soda and

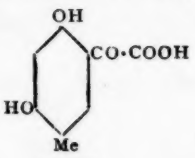


acidification again led to decarboxylation with the formation of (XV). Modified experimental conditions for the preparation of (XIX) are being examined.

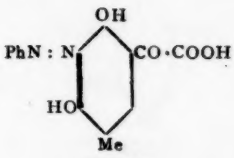
In attempting to separate monoazo and disazo dyes obtained by coupling diazonium salts with citrinin and with resorcinol derivatives by chromatographic adsorption on alumina, it was found that a monoazo dye (*e.g.*, 4-benzeneazoresorcinol) appeared in the upper part of the column,

being more strongly adsorbed than the corresponding disazo dye such as 2:4- or 4:6-*bis*benzeneazoresorcinol. This is in sharp contrast to the behaviour of the azo dyes of the usual type used in dyeing wool and cotton, which were examined by Ruggli and Jensen,[21] and in which the adsorbability increased with the number of azo groups. The explanation appears to be that while the azo groups were the determining factor in the soluble dyes containing sodium sulphonate groups studied by Ruggli and Jensen, the hydroxyl groups also play a part in the case of the azoresorcinols, so that the disazo compounds in which both the hydroxyl groups are chelated with azo groups are less strongly adsorbed. It was further observed that from a chloroform solution of a mixture of 2-benzeneazo-4-methylresorcinol (XV) and 6-benzeneazo-4-methylresorcinol (XIII) chromatographed on an alumina column, (XIII) was retained at the top of the column and (XV) was very weakly adsorbed. The azo group in (XV) acts as a receptor for two hydrogen bonds, so that neither of the hydroxyl groups is active in adsorption on alumina. In its behaviour during chromatographic adsorption the monoazo dye from Product A and diazotized aniline resembled (XIII) rather than (XV).

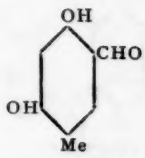
When 2:4-dihydroxytolyl-5-glyoxylic acid (XXII), prepared by condensing 4-methylresorcinol with ethyl cyanoformate according to Hunsberger and Amstutz,[20] was treated in alkaline solution with diazotized aniline, coupling took place in the γ-position of the resorcinol nucleus without replacement of the glyoxylic acid group, the product being (XXIII). On the other hand, the aldehyde group in (XXIV) was ejected on coupling with diazotized aniline.



(XXII)

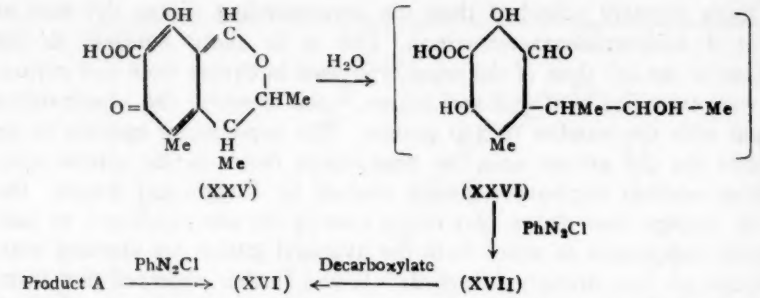


(XXIII)



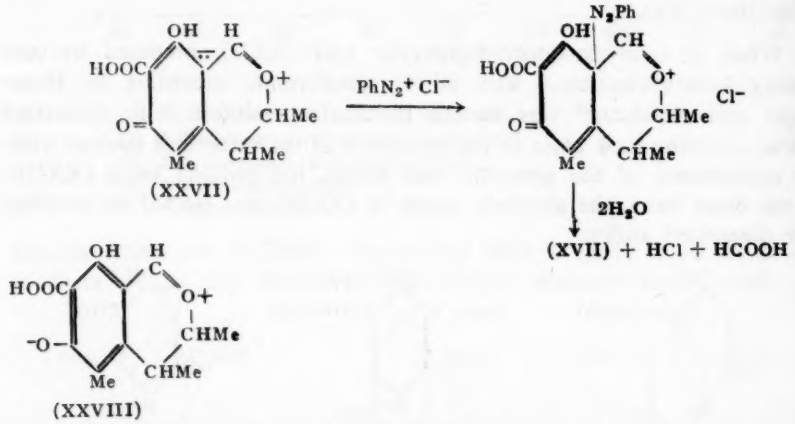
(XXIV)

The structure (XXV) for citrinin, proposed by Robertson, *et al.*,[22] while our work was in progress, is more in conformity with its behaviour on treatment with diazonium salts than the slightly different structure (X) suggested by us earlier. If the first stage of the reaction is assumed to be hydrolytic fission of the heterocyclic ring, resulting in the formation of the resorcyl-4-aldehyde-2-carboxylic acid (XXVI), coupling would take place in the first instance by the displacement of the aldehyde group; decarboxylation of the monoazo dye (XVII) would then yield the 4-benzeneazoresorcinol (XVI),



identical with the monoazo dye obtained by coupling Product A with diazotized aniline.

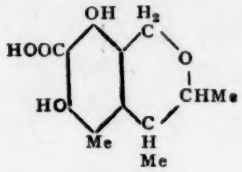
Prior hydrolysis of citrinin to the aldehyde (XXVI) is improbable under the conditions of diazonium coupling. An alternative mechanism is a direct electrophilic attack of the diazonium cation on the coupling site which has a high electron density in the resonance structure (XXVII) for citrinin.



The colour and comparative stability of citrinin may be associated with the resonance of the molecule among such structures as (XXV), (XXVII) and (XXVIII).

Hetherington and Raistrick have recorded that on reduction with nascent hydrogen (zinc and acetic acid) citrinin gave a colourless dihydroxy compound ($C_{13}H_{16}O_5$), which was readily reoxidised to citrinin by atmospheric oxygen. Robertson, *et al.*, have observed "the formation of a stable dihydro derivative with simultaneous aromatization"; the conditions under which the reduction was effected have not been stated. They

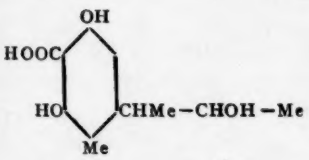
regard the blue ferric reaction of the dihydro derivative, which is characteristic of γ-resorcylic acids, as supporting the structure (XXIX). When



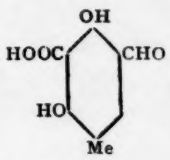
(XXIX)

citrinin was hydrogenated in alcoholic solution at 40 lbs. pressure in presence of Raney nickel, the product gave the characteristic blue colour with ferric chloride. When the glyoxylic acid (XXII) was similarly reduced, the product was found to exhibit a blue colour with ferric chloride very similar to the γ-resorcylic acid colouration, but the colouration was less permanent than in the case of γ-resorcylic acid and of the reduction product of citrinin.

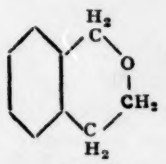
The ultimate proof for the constitution must rest on the synthesis of citrinin, which we are now attempting. It has been found that the action of boiling potassium bicarbonate solution on Product A gives the γ-resorcylic acid (XXX) as indicated by the characteristic blue colouration, and an aldehyde synthesis on this carboxylic acid (and its ester) is being studied. Another approach we are making is the condensation of 4-methylresorcyl-6-aldehyde and its 2-carboxylic acid (XXXI) with 2:3-butylene glycol,



(XXX)



(XXXI)



(XXXII)

since it is probable that such a mechanism is involved in the phytochemical synthesis of citrinin. We have also undertaken synthetical experiments in the *iso*chromane series. *Iso*chromane (XXXII) and its derivatives have been stated[23] to be useful in the preparation of dyestuffs, medicinals and perfumes, and three synthetic routes have been outlined[23, 24] in the case of the parent compound (XXXII). An *iso*chromene derivative, isobenzpyrylium ferrichloride, has been prepared by Blount and Robinson[25] by the action of hydrogen chloride and ferric chloride on homophthalaldehyde.

Experimental

Preparation of citrinin.—Czapex-Dox glucose solution[3] was inoculated in Roux flasks with an aqueous suspension of the spores of *Penicillium citrinum* Thom., the strain being isolated from Manohar's mixed culture. After 4 days of incubation at room temperature (26–28°), a white growth with a yellowish colour underneath was visible. The colour of the medium gradually changed from pale yellow to bright canary yellow during an incubation period of 15 days at the end of which the upper surface of the mycelium was dark grey while the under-surface was yellow. The metabolite solution was then filtered and acidified with 10 c.c. of 5N hydrochloric acid per l. of the solution, when a bright yellow precipitate was obtained. Crystallization from alcohol gave long yellow needles, m.p. 171·5° (decomp.). It was observed that prolonged boiling of an alcoholic solution lowered the yield of pure crystalline citrinin. An average yield of 1 g. per l. of medium was obtained.

Products A and B.—A typical hydrolysis of citrinin (5·0 g.), according to Hetherington and Raistrick, by refluxing with 2N sulphuric acid (100 c.c.) for 5 hours gave tarry matter (0·8 g.), Product A (1·2 g.), Product B (0·9 g.) and a material (0·6 g.) highly soluble in chloroform. It was noticed that Product B was produced in relatively large amounts in our experiments. Product A on recrystallization from chloroform was obtained in colourless prisms, m.p. 129–30°. Product B crystallized from ethyl acetate in colourless prisms melting at 169–70°. An aqueous solution of Product A gives with aqueous ferric chloride a pale blue colouration; Product B gives a similar but somewhat more intense colouration.

Product C.—Fusing Product A with potassium hydroxide as described by Hetherington and Raistrick, a phenol was obtained which crystallized from benzene in long colourless needles, m.p. 68–69°. On drying at 105° for 2 hours the substance lost one molecule of water (loss of weight 11·2. $C_9H_{12}O_2$, H_2O requires H_2O, 10·6%). The anhydrous substance melted at 98–99°. A light blue colouration is given with ferric chloride in aqueous solution, but none in alcoholic solution.

Coupling of citrinin with diazotized aniline.— (1) Aniline (0·74 g.; 0·08 mole) was diazotized at 0° by means of concentrated hydrochloric acid (2·2 c.c.), water (2·2 c.c.) and sodium nitrite (0·52 g.), and after adding sodium acetate (2·5 g.), the diazonium solution was added to a mechanically stirred solution of citrinin (2·0 g.; 0·08 mole) in 5% sodium hydroxide solution (50 c.c.) cooled with ice and salt. The reaction mixture was stirred for about 5 minutes and acidified with dilute hydrochloric acid. The reddish

orange dye was filtered, washed and dried (1·6 g.). The crude dye was dissolved in ether and the solution was extracted successively with 5% sodium bicarbonate, 5% sodium carbonate and 5% caustic soda solutions. On acidifying the alkaline extracts most of the dye (1·4 g.) was recovered from the sodium hydroxide extract. This dye on crystallization from alcohol gave red needles (0·38 g.), m.p. 183° (decomp.) (Found: C, 62·9; H, 6·0; N, 8·2. $C_{18}H_{20}O_5N_2$ (XI or XVII) requires C, 62·7; H, 5·8; N, 8·1%. $C_{19}H_{18}O_5N_2$ (benzeneazo derivative of X) requires C, 64·4; H, 5·1; N, 7·9%). The substance is sparingly soluble in sodium bicarbonate solution, but dissolves readily in caustic soda solution. The solution in concentrated sulphuric acid is orange red in colour. On treating the dye (0·1 g.) with boiling 2N sulphuric acid for 5 hours, it is recovered unchanged. It is also unaffected on boiling with water for 24 hours.

The mother-liquor from the crystallization of the dye, m.p. 183°, was evaporated, and the residue when repeatedly crystallized from 20% alcohol gave orange needles, m.p. 190° (Found: C, 68·3; H, 6·4; N, 9·7. $C_{17}H_{20}O_3N_2$ requires C, 68·0; H, 6·6; N, 9·3%).

The ether layer left after the extractions with alkali in working up the dye, m.p. 183°, was orange coloured, and on evaporation gave a crystalline residue which on recrystallization from alcohol yielded lustrous red needles, m.p. 205° (Found: C, 68·2; H, 5·8; N, 14·6. $C_{23}H_{24}O_3N_4$ requires C, 68·3; H, 5·9; N, 13·9%). This dye was found to be identical in its m.p. and mixed m.p. with the *bis*benzeneazo derivative of Product A.

Decarboxylation of the dye (XVII), m.p. 183°.—The dye (0·1 g.) mixed with anhydrous glycerine (5 c.c.) was heated in a glycerine bath. At about 144° the dye went into solution with a copious evolution of gas. The temperature was then raised to 185–8° and heating continued for 5 minutes, when no more bubbles appeared. The solution was cooled, diluted with water, and the precipitate filtered. The product on repeated crystallization from 20% alcohol was obtained in orange needles, m.p. 190° (Found: C, 68·4; H, 6·4; N, 9·7. $C_{17}H_{20}O_3N_2$ requires C, 68·0; H, 6·6; N, 9·3%). There is no depression in melting point when the substance is mixed with the dye, m.p. 190°, isolated from the product of the coupling of citrinin with diazotized aniline. The m.p. is also undepressed by admixture with the monobenzeneazo derivative (XVI) of Product A. The substance dissolves in sodium carbonate solution and in concentrated sulphuric acid with an orange colour.

(2) Coupling citrinin (0·3 g.; 0·0012 mole) in 10% sodium carbonate solution (15 c.c.) and 10% sodium acetate solution (15 c.c.) with diazotized

aniline (4 mols.), during one hour, and carrying out the separation as in the previous experiment, most of the product was recovered from the sodium hydroxide extract. This dye, on crystallization from alcohol, was obtained in lustrous reddish orange needles (0·06 g.), m.p. 183° (decomp.) (Found: N, 8·2). The ethereal layer after extraction by alkali was deep red in colour and on evaporation left a red crystalline residue. Recrystallization from alcohol gave red needles (0·12 g.), m.p. 205° (Found: N, 14·7).

The aqueous filtrate, on keeping overnight in a refrigerator, deposited a brown substance which crystallized from alcohol in chocolate coloured needles, m.p. 131°, identified as 2: 4-*bis*benzeneazophenol (Found: N, 18·4. $C_{18}H_{14}ON_4$ requires N, 18·5%).

(3) Coupling as in (2), but for 4 hours or more, the monoazo and disazo derivatives of Product A (m.p. 190° and m.p. 205° respectively) were obtained in relatively large yields with a decrease in the yield of the azo carboxylic acid, m.p. 183°.

Coupling of citrinin with diazotized o-chloroaniline.—A solution of diazotized *o*-chloroaniline, prepared from *o*-chloroaniline (0·13 g.; 0·001 mole) was treated with excess of sodium acetate, and then added at 0–5° to a solution of citrinin (0·2 g.; 0·0008 mole) in alcohol (30 c.c.). After 30 minutes, the bright red dye was filtered, washed and dried (0·25 g.). Crystallization from alcohol gave red-orange plates with golden lustre, m.p. 184° (decomp.) (Found: C, 56·7; H, 5·0; N, 7·1. $C_{18}H_{19}O_5N_2Cl$ requires C, 57·1; H, 5·0; N, 7·4%. $C_{19}H_{17}O_5N_2Cl$ requires C, 58·7; H, 4·4; N, 7·2%).

Coupling of citrinin with diazotized 2: 5-*dichloroaniline.*—A diazonium solution prepared from 2: 5-dichloroaniline (0·65 g.; 0·004 mole) was added to a solution of citrinin (0·25 g.; 0·001 mole) in 10% sodium carbonate solution (10 c.c.) and 10% sodium acetate solution (25 c.c.). After one hour the orange dye was filtered, washed and dried (0·3 g.). The ether soluble part of the dye was extracted successively with 5% solutions of sodium bicarbonate, sodium carbonate and sodium hydroxide solutions. On acidification of the alkaline extracts most of the dye was obtained in the sodium hydroxide extract. The dye on crystallization from chloroform gave reddish orange leaflets with golden lustre, m.p. 200–1° (decomp.) (Found: C, 51·7; H, 4·6; N, 6·6; Cl, 17·3; Neutralization equivalent 420. $C_{19}H_{16}O_5N_2Cl_2$ requires C, 53·9; H, 3·8; N, 6·6; Cl, 16·8%; Neutralization equivalent 423. $C_{18}H_{18}O_5N_2Cl_2$ requires C, 52·3; H, 4·36; N, 6·8; Cl, 17·2%; Neutralization equivalent 413).

Coupling of Product A with diazotized aniline (1).—The diazonium solution prepared from aniline (0·4 g.; 0·004 mole) in the usual manner was added to a solution of Product A (0·2 g.; 0·001 mole) in 10% sodium carbonate solution (5 c.c.) and 10% sodium acetate (30 c.c.). After 1 hour the dye was filtered, washed and dried (0·4 g.). Crystallized from alcohol, the lustrous red needles had m.p. 205° (Found: C, 68·1; H, 5·8; N, 14·6. $C_{23}H_{24}O_3N_4$ requires C, 68·3; H, 5·9; N, 13·9%). The substance is therefore the *bis*benzeneazo derivative of Product A. The m.p. is not depressed when admixed with the dye, m.p. 205°, obtained in the coupling of citrinin with diazotized aniline.

(2) To a mechanically stirred solution of Product A (0·588 g.; 0·001 mole) in water (30 c.c.) and sodium acetate (4 g.) was added a diazonium solution prepared from aniline (0·28 g.; 0·001 mole). The reaction mixture was stirred for about 5 minutes, acidified with dilute hydrochloric acid, and the precipitated dye filtered, washed and dried (0·45 g.). The dye was dissolved in benzene (30 c.c.) and chromatographed on a column of standardized alumina. Using the same solvent for development of the chromatogram, two bands appeared: an upper orange-coloured band and a lower, but contiguous, deep red band. On running in a mixture of benzene and alcohol (50: 50), the lower band was eluted, while the upper band was retained by the alumina. The alcohol-benzene percolate on evaporation gave a red crystalline residue, which crystallized from alcohol in red needles (0·06 g.), m.p. 205°, identical with the disazo dye obtained earlier from Product A. The bright orange band was then eluted by digesting the adsorbent with boiling alcohol repeatedly. The dye thus recovered crystallized from 20% alcohol in orange needles (0·1 g.), m.p. 190° (Found: C, 68·3; H, 6·4; N, 9·7. $C_{17}H_{20}O_3N_2$ requires C, 68·0; H, 6·6; N, 9·3%). The substance is therefore a monobenzeneazo derivative of Product A. The m.p. is not depressed by admixture with the dye, m.p. 190°, obtained by coupling citrinin with diazotized aniline, or with the product of decarboxylation of the dye, m.p. 183°, also obtained by coupling citrinin with diazotized aniline.

Coupling of Product A with diazotized o-chloroaniline.—Using two mols. of *o*-chloroaniline for one of Product A, the orange dye was the disazo derivative, which crystallized from glacial acetic acid in bunches of fine lustrous needles, m.p. 278° (Found: C, 58·1; H, 4·5; N, 12·4. $C_{23}H_{22}O_3N_4Cl_2$ requires C, 58·3; H, 4·65; N, 11·8%).

Coupling of Product A with 2: 5-*dichloroaniline.*—Using 4 mols. of 2: 5-dichloroaniline for one of Product A, the disazo dye crystallized from

chloroform in fine red needles, m.p. 283–4° (Found: N, 10·3. $C_{23}H_{20}O_3N_4Cl_4$ requires N, 10·3%).

Coupling of Product A with 5-nitro-o-anisidine.—The disazo dye crystallized from nitrobenzene in microscopic red rods, which shrank at 320°, but did not melt up to 350° (Found: N, 15·2. $C_{25}H_{20}O_9N_6$ requires N, 15·2%).

Coupling of Product C with diazotized aniline.—A diazonium solution prepared from aniline (0·37 g.; 0·004 mole) was added at 0–5° to a stirred solution of Product C (0·15 g.; 0·001 mole) in 2% sodium hydroxide solution (20 c.c.). After 30 minutes, the product was collected (0·35 g.), and crystallization from alcohol gave shining red needles, m.p. 171° (Found: C, 69·7; H, 5·6; N, 15·4. $C_{21}H_{20}O_2N_4$ requires C, 70·0; H, 5·5; N, 15·6%). The dye gives a red orange colouration with 10% caustic soda solution.

Coupling of Product C with diazotized o-chloroaniline.—The disazo dye crystallized from alcohol in red needles, m.p. 228° (Found: N, 13·2. $C_{21}H_{18}O_2N_4Cl_2$ requires N, 13·1%).

The disazo dye from 2: 5-dichloroaniline crystallized from glacial acetic acid in red needles, m.p. 255–7° (Found: N, 11·4. $C_{21}H_{16}O_2N_4Cl_4$ requires N, 11·2%). The disazo dye from diazotized 5-nitro-*o*-anisidine crystallized from glacial acetic acid in crimson red microscopic needles, m.p. 274–5° (Found: N, 16·4. $C_{23}H_{22}O_8N_6$ requires N, 16·5%). The colouration in concentrated sulphuric acid is purple.

2: 4- *and* 4: 6-*bis-Benzeneazoresorcinol.*—The disazo dyes from resorcinol and diazotized aniline were prepared in the known manner.[26] With 10% caustic soda solution 2: 4-*bis*benzeneazoresorcinol gives an orange colouration, while the 4: 6-isomer gives a bordeaux-red colouration. With concentrated sulphuric acid both give red-orange colourations.

2: 4-*bis-Benzeneazo-5-methyl-6-ethyl resorcinol.*—5-Methyl-4-ethylresorcinol (VI) (0·05 g.), m.p. 79–82°, prepared by the method of Shah and Robinson,[16] was dissolved in alcohol (10 c.c.) and 10% sodium carbonate solution (5 c.c.) and on coupling with diazotized aniline gave a dye (0·12 g.) which crystallized from alcohol in red needles melting at 188° (Found: N, 15·5. $C_{21}H_{20}O_2N_4$ requires N, 15·6%). The m.p. is depressed when admixed with the *bis*benzeneazo derivative of Product C. The substance gives a red-orange colouration with 10% caustic soda and an orange with concentrated sulphuric acid.

4: 6-*bis-Benzeneazo-2-ethylresorcinol.*—Coupling 2-ethylresorcinol[27] in 10% sodium hydroxide solution with excess of diazotized aniline, the dye

crystallized from glacial acetic acid in deep red-violet needles, m.p. 162° (Found: N, 15·8. $C_{20}H_{18}O_2N_4$ requires N, 16·2%). It gives a bordeaux-red colouration with 10% caustic soda solution, and a deep red with concentrated sulphuric acid.

2: 4-*bis*-*Benzeneazo*-6-*acetylresorcinol*.—To a mechanically stirred solution of resacetophenone (0·6 g.; 0·004 mole) in 10% sodium hydroxide solution (10 c.c.) a diazonium solution prepared from aniline (1·5 g.; 0·016 mole) containing excess of sodium acetate was added. The dye crystallized from glacial acetic acid in fine red needles, m.p. 220–1° (Found: N, 15·5. $C_{20}H_{16}O_3N_4$ requires N, 15·6%). The *diacetyl* derivative crystallised from alcohol in red needles, m.p. 148° (Found: N, 12·8. $C_{24}H_{20}O_5N_4$ requires N, 12·6%).

4: 6-*bis*-*Benzeneazo*-2-*acetylresorcinol*.—Coupled in alkaline solution with excess of diazotized aniline, 2-acetylresorcinol gave a dye which crystallized from alcohol in shining deep red rods, m.p. 169–70° (Found: N, 15·5. $C_{20}H_{16}O_3N_4$ requires N, 15·6%).

6-*Benzeneazo*-4-*methylresorcinol* (*XIII*).—To a stirred solution of 4-methylresorcinol (0·5 g.; 0·004 mole) in 10% sodium acetate solution (30 c.c.) was added a diazonium solution obtained from aniline (0·37 g.; 0·004 mole). The orange dye was collected after stirring the reaction mixture for half an hour. Crystallization from 50% alcohol gave thick scarlet-red needles, m.p. 180° (Found: C, 68·2; H, 5·0; N, 12·4. $C_{13}H_{12}O_2N_2$ requires C, 68·4; H, 5·3; N, 12·3%). The insoluble residue crystallized from 95% alcohol in orange needles, m.p. 212°, and was found to be the disazo derivative[29] (Found: N, 17·1. $C_{19}H_{16}O_2N_4$ requires N, 16·9%).

2-*Benzeneazo*-4: 6-*diethylresorcinol* (*XIV*).—This was prepared according to Shah and Mehta.[28]

2: 4-*Dihydroxytolyl*-5-*glyoxylic acid* (*XXII*)—was prepared from 4-methylresorcinol (m.p. 104°) (5·0 g.) and ethyl cyanoformic ester (4·1 c.c.) after the method of Hunsberger and Amstutz.[20] The acid crystallized from water acidulated with a drop of hydrochloric acid in golden yellow laminæ (3·1 g.; m.p. 167°) (decomp.). The crystals lose their lustre and change in colour to brown on drying in an air oven at 110°. (Found: C, 54·6; H, 4·4. $C_9H_8O_5$ requires C, 55·1; H, 4·1%.) The alcoholic solution gives a red brown colouration with ferric chloride.

Coupling of (*XXII*) *with diazotized aniline; preparation of* (*XXIII*).—The diazonium solution prepared from aniline (0·28 g.; 0·003 mole) was gradually added to a stirred solution of 2: 4-dihydroxytolyl-5-glyoxylic acid

(0·59 g.; 0·003 mole) in 5% aqueous caustic soda (20 c.c.). After 15 minutes, the reaction mixture was acidified with dilute hydrochloric acid and the orange red dye was filtered, washed and dried (0·54 g.); the dye crystallized from water in shining red needles, m.p. 183° (decomp.). The crystals lose their lustre on drying at 105°. (Found: C, 59·7; H, 3·9; N, 9·4. $C_{15}H_{12}O_5N_2$ requires C, 60·0; H, 4·0; N, 9·3%).

Methyl 4-methylresorcinol-6-carboxylate.—4-Methyl-resorcinol-6-carboxylic acid (XX) (1·0 g.) was refluxed with absolute methanol (4 c.c.) and a few drops of concentrated sulphuric acid for 10 hours. On dilution with water, the crystalline precipitate was taken up in ether and extracted with 5% sodium bicarbonate solution. Evaporation of the ether solution and crystallization from aqueous alcohol gave colourless needles (0·6 g.), m.p. 121° (Found: C, 59·3; H, 5·6. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%). The substance gives a bluish violet colour with alcoholic ferric chloride.

Methyl 2-benzeneazo-4-methylresorcinol-6-carboxylate (XXI) and 2-Benzeneazo-4-methylresorcinol (XV).—Methyl 4-methylresorcinol-6-carboxylate (0·5 g.) was dissolved in 2% caustic soda solution (30 c.c.) and treated with the diazonium solution prepared from aniline (0·25 g.). The mixture was acidified after 5 minutes, and the precipitate filtered, washed and dried (0·7 g.). Crystallization from alcohol gave red needles, m.p. 172° (Found: N, 10·1. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

On refluxing the dye (XXI) (0·2 g.) with 8% alcoholic caustic potash (25 c.c.) for 3 hours on a water-bath and acidifying, a yellow substance (XV) was obtained, which on crystallization from alcohol (norit) gave yellow needles, m.p. 176° (Found: C, 68·2; H, 5·0; N, 12·3. $C_{13}H_{12}O_2N_2$ requires C, 68·4; H, 5·3; N, 12·3%).

When the ether solution of a 2-benzeneazo derivative of resorcinol is extracted with 2% sodium carbonate solution, the aqueous layer is colourless. On the other hand, in the case of the 4-benzeneazoresorcinols the aqueous extract is bright orange in colour and yields the azo dye on acidification.

Separation of (XIII) and (XV) by chromatographic adsorption.—A solution of 2-benzeneazo-4-methylresorcinol (XV) (0·003 g.) and 4-benzeneazo-6-methylresorcinol (XIII) (0·015 g.) in chloroform (15 c.c.) was chromatographed on standardised alumina (Savory and Moore). A scarlet band of 0·5 cm. height was formed at the top, while a yellow percolate moved downwards. On developing with chloroform and benzene (1:1), the scarlet band remained adsorbed and (XV) was recovered from the chloroform-benzene percolate. By separating the scarlet layer of alumina and boiling with alcohol, (XIII) was obtained.

4-Benzeneazoresorcinol-2-carboxylic acid (*XVIII*).—To a stirred solution of γ-resorcylic acid (0·31 g.; 0·002 mole) in alcohol (30 c.c.) and sodium acetate (1 g.) was added the diazonium solution from aniline (0·19 g.; 0·002 mole). On leaving overnight in a refrigerator and diluting with water, a red dye was precipitated which crystallized from alcohol in red needles, m.p. 191° (Found: C, 60·7; H, 4·2; N, 11·2. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·8; N, 10·9%). The dye is partly decarboxylated on boiling with 2N sulphuric acid or water under the conditions described for the mono-azo carboxylic acid from citrinin.

4: 6-*Dimethoxy-o-toluic acid* (*VIII*).—1-Methyl-1: 2-dicarbethoxy-Δ^2-cyclohexane-4: 6-dione, obtained by condensation of ethyl α-acetylpropionate with ethyl chlorofumarate was hydrolysed to obtain 4: 6-dihydroxy-*o*-toluic acid according to the method of Woodward and Reed.[18] The acid was methylated with excess of dimethyl sulphate and aqueous caustic soda in the usual manner. At the end of the reaction, the alkaline solution was heated on the water-bath for 30 minutes and acidified. Crystallization of the precipitate from water gave shining colourless needles, m.p. 157–8° (Found: C, 61·3; H, 6·3. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%). The dimethoxy acid as well as the parent dihydroxy acid, on warming with concentrated sulphuric acid, give a bordeaux red colouration (anthrachrysone reaction).

Summary

The constitution (I) proposed in 1931 by Coyne, Raistrick and Robinson for citrinin, an antibiotic produced by *Penicillium citrinum*, and the structures assigned to the product (A) of the sulphuric acid hydrolysis of citrinin and the dialkylresorcinol (C) obtained by alkali fusion of (A), have been shown to be untenable in view of their behaviour towards diazonium salts. The dialkylresorcinol (C) is 4-methyl-5-ethylresorcinol, and not 4-methyl-2-ethylresorcinol. From the orientation of the alkyl groups in (C) and the experimental results of Hetherington and Raistrick it follows that Product (A) is 4-methyl-5-(1-methyl-2-hydroxy)-propylresorcinol (IX), as suggested by Cram. Two alternative structures (X and XXV), which are both derived from an isochromane system and which differ from each other only in the position of the carboxyl group, are discussed; the action of diazonium salts on citrinin and on Product (A) is better explained by (XXV).

In the chromatographic adsorption of *mono-* and *bis*-benzeneazoresorcinols on an alumina column, 4-benzeneazoresorcinol is more strongly adsorbed than 2: 4- or 4: 6-*bis*benzeneazoresorcinol, while Ruggli and Jensen have observed that the adsorbability of the azo dyes studied by them increased with the number of azo groups. 2-Benzeneazo-4-methylresorcinol

is more weakly adsorbed than 6-benzeneazo-4-methylresorcinol. These effects are ascribed to chelation between the azo and hydroxyl groups.

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THE PHYSICAL IDENTITY OF ENANTIOMERS

Part VIII. The Magnetic Susceptibilities of *Dextro*, *Laevo* and *Racemic* Forms of Camphor-β-Sulphonates of Nitrogen Bases

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According to the Pasteur's principle of Molecular Dissymmetry the dextro and lævo forms of a compound possess identical scalar properties.* Previous investigations[1] on magnetic susceptibilities of dextro and lævo isomers showed that their values were equal within the limits of experimental error and thus support Pasteur's principle. The present investigation was undertaken to further establish the validity of this principle as well as to study the effect on the magnetic susceptibility of the change of the valency of nitrogen from 3-covalent to 4-covalent state in the formation of substituted ammonium-camphor-β-sulphonates. The magnetic susceptibilities of the racemic modifications were also studied since a comparison of the values of susceptibilities of the racemic forms with those of their dextro and lævo isomers might throw light on the nature of the racemic combination. If the racemic modification were an equimolecular mixture of *d*- and *l*-components, there should be no difference in the values of magnetic susceptibilities, whereas if the racemic form were a compound its magnetic susceptibility might be different from that of *d*- and *l*-form.

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* Campbell (*Trans. Faraday Soc.*, 1930, **26**, 560 ; *J. Amer. Chem. Soc.*, 1931, **53**, 1661) reported slight, but distinct differences in the rotatory power and other physical properties of the *dextro* and *lævo*-forms of mandelic and camphoric acids and disputed the validity of Pasteur's principle of molecular dissymmetry. Körtum (*Ber.*, 1931, **64 B**, 1506) in the case of mandelic acids (*d*- and *l*-) showed that if the preparations are sufficiently purified, there are no measurable differences in the rotatory power of the optically active and opposite forms. One of us (Singh, B. K., Mahanti, I., *Proc. Ind. Acad. Sci.*, 1935, **2**, 378 ; *Curr. Sci.*, 1935, **3**, 420) showed in 1935 that the rotatory dispersions of the *d*- and *l*-camphoric acids are identical throughout the visible spectrum ($\lambda = 4358$ to 6709 A°.U.). In spite of these and other rigid proofs, Bowden wrote in 1938 "The supposed identity of *d*- and *l*-forms is really an unproved assumption " (The Phase Rule and Phase Reactions ; foot-note, p. 191), and quoted the above mentioned alleged differences for mandelic acids noted by Campbell. In this paper we have adduced more evidence from magnetic measurements in support of Pasteur's great generalisation.

Experimental

The *l*- and *dl*-forms of camphor-β-sulphonic acids were prepared in the same way as Reychler's acid[2] (*d*-camphor-β-sulphonic acid). The camphor-β-sulphonates of *o*-, *m*- and *p*-nitranilines, pyridine, ammonia, *p*-aminobenzenesulphonamide and aniline were prepared according to methods described in previous communications.[3]

The magnetic susceptibility measurements were carried out by a modified form of Guoy's Balance. The working of the apparatus was checked by making determinations of magnetic susceptibilities of compounds with known values. In Table I are recorded some of the results. Water with the value of $\chi - 0{\cdot}720 \times 10^{-6}$ was taken as a standard for these measurements.

Table I

Substance	$\chi \times 10^6$ per gm.		Percentage deviation
	Experimental mean of three observations	International Critical Tables	
Potassium chloride ..	0·515	0·516	0·2
Naphthalene ..	0·718	0·717	0·2
Camphoric anhydride ..	0·622	0·620	0·3
1 : 3 : 5-trinitro-benzene ..	0·351	0·352	0·3
Ethyl alcohol ..	0·744	0·744	0·0

For the sake of comparison the values of diamagnetic susceptibilities of bases were also determined. In Table II are recorded the values of gram (χ) and gram molecular (χ_M) susceptibilities of compounds investigated. Table III gives the observed values (O) of χ_M and those calculated (C) from the sum of their components; the differences (O−C) are also recorded.

Discussion

The values of magnetic susceptibilities of dextro and lævo isomers agree within the limits of the experimental error, and thus confirm Pasteur's law. The values of the racemic forms do not, in general, differ appreciably from those of the active forms beyond experimental error. However, in the case of *p*-aminobenzenesulphonamido-camphor-β-sulphonates the diamagnetic susceptibility of the racemic form is different from that of the dextro and the lævo isomer (*vide* Table II) and if this difference is genuine, it indicates that the racemic modification is a true *dl*-compound. It has been shown previously[4] that all the racemic modifications investigated in this paper are

TABLE II

	Compound	Molecular weight	$\chi \times 10^6$	per gram mol. $\chi \times 10^6$
1	Aniline ..	93	0·692	64·36
2	Ortho-nitroaniline ..	138	0·506	69·84
3	Meta-nitroaniline ..	138	0·503	69·42
4	Para-nitroaniline ..	138	0·478	65·97
5	Pyridine ..	79	0·623	49·21
6	*p*-Aminobenzene sulphonamide ..	172	0·466	80·15
7	*d*-Camphor-*β*-sulphonic acid ..	232	0·584	135·5
8	*l*-Camphor-*β*-sulphonic acid ..	232	0·584	135·5
9	*dl*-Camphor-*β*-sulphonic acid ..	232	0·586	135·9
10	*o*-Nitroanilino-*d*-S*. $2H_2O$ ..	406	0·490	198·9
11	,, ,, *-l-* ,, ,, ..	406	0·493	200·1
12	,, ,, *-dl-* ,, ,, ..	406	0·485	196·9
13	*m*-Nitranilino-*d*- S ..	370	0·553	204·6
14	,, ,, *-l-* ,, ..	370	0·549	203·2
15	,, ,, *-dl-* ,, ..	370	0·551	203·9
16	*p*-Nitranilino-*d*- S. $3H_2O$ ..	424	0·505	214·1
17	,, ,, *-l-* ,, ,, ..	424	0·502	212·8
18	,, ,, *-dl-* ,, ,, ..	424	0·496	210·3
19	Pyridino-*d*- S ..	311	0·597†	185·7
20	,, *-l-* ,, ..	311	0·590†	183·5
21	,, *-dl-* ,, ..	311	0·585†	182·0
22	*p*-Aminobenzenesulphonamido-*d*- S ..	404	0·505	204·0
23	,, ,, *-l-* ,, ..	404	0·508	205·2
24	,, ,, *-dl* ,, ..	404	0·488	197·2
25	Anilino-*dl*- S ..	325	0·584	189·8
26	Ammonium-*d*- S ..	249	0·566	140·9

* S denotes camphor-*β*-sulphonic acid.

† Values actually determined in solution (aqueous) and calculated for solid.

TABLE III

	Compound	$\chi \times 10^6$ per gram mol. (observed) O	$\chi \times 10^6$ per gram mol. (calculated) C	O−C
1	*o*-Nitroanilino.*d*- S*. $2H_2O$ ..	198·9	231·26	−32·36
2	,, ,, *-l-* ,, ,, ..	200·1	231·26	−31·16
3	,, ,, *-dl-* ,, ,, ..	196·9	231·66	−34·76
4	*m*-Nitranilino-*d*- S ..	204·6	204·92	− 0·32
5	,, ,, *-l-* ,, ..	203·2	204·92	− 1·72
6	,, ,, *-dl-* ,, ..	203·9	205·32	− 1·42
7	*p*-Nitranilino-*d*-S. $3H_2O$ ..	214·1	240·35	−26·25
8	,, ,, *-l-* ,, ,, ..	212·8	240·35	−27·55
9	,, ,, *-dl-* ,, ,, ..	210·3	240·75	−30·45
10	Pyridino-*d*- S ..	185·7	184·71	+ 0·99
11	,, *-l-* ,, ..	183·5	184·71	− 1·21
12	,, *-dl-* ,, ..	182·0	185·11	− 3·11
13	*p*-Aminobenzenesulphonamido-*d*- S	204·0	215·67	−11·67
14	,, ,, *-l-* ,,	205·2	215·67	−10·47
15	,, ,, *-dl-* ,,	197·2	216·05	−18·85
16	Anilino-*dl*-S ..	189·8	200·26	−10·46
17	Ammonium-*d*-S ..	140·9	149·5	− 8·6

* *S* denotes camphor-*β*-sulphonic acid.

true *dl*-compounds. The present studies indicate that in general the linkages involved in compound formation in the case of racemic modifications are such as do not effect the diamagnetic susceptibility to any appreciable extent.

Effect of Position of Isomerism on Magnetic Susceptibility

The sequence of magnetic susceptibility of position isomerides of nitroanilines is $o > m > p$. On the other hand, the decreasing order of gram susceptibilities (χ) of *o*-, *m*- and *p*-nitranilinocamphor-β-sulphonates is $m > p > o$. Bhatnagar and collaborators[5] in their study of *o*-, *m*- and *p*-cresyl ethers and *o*- and *p*-phenetidine had come to the conclusion that the ortho should be more diamagnetic than the meta and the para isomerides. Their rule is obviously untenable in the case of *o*-, *m*- and *p*-nitranilinocamphor-β-sulphonates where the meta isomer having no water of crystallisation posesesses greater gram susceptibility than either ortho or para isomerides which contain water of crystallisation. These studies, therefore, show that no definite rule is observed in regard to the sequence of magnetic susceptibility of position isomerides.

An examination of the values given in Table III indicates that the observed values (O) of gram moleculer susceptibilities (χ_M) of camphor-β-sulphonates are generally less than the sum (C) of gram molecular susceptibilities of their components. On Pascal's law the differences, O−C, should be nearly constant since salt formation involves a change of 3-covalent nitrogen to 4-covalent nitrogen in every case. The different camphor-β-sulphonates examined in this paper can be divided into three groups, *viz.*, (i) where the difference O−C is negligible as in the case of camphor-β-sulphonates of pyridine and *m*-nitraniline, (ii) where O−C is about $10{\cdot}5 \times 10^{-6}$ as in the case of salts of ammonia, aniline and *p*-aminobenzenesulphonamide and (iii) where O−C varies from $26{\cdot}25 \times 10^{-6}$ to $34{\cdot}76 \times 10^{-6}$ as in the cases of *o*- and *p*-nitranilinocamphor-β-sulphonates. These results indicate that the formation of salts of camphor-β-sulphonic acid with nitrogen bases involves not merely a change of 3-covalent nitrogen to 4-covalent nitrogen but that there are other factors also which influence the value of diamagnetic susceptibility.

Summary

1. The magnetic susceptibilities of *d*- and *l*-isomers of camphor-β-sulphonic acids and some of their salts have been measured and are found to be equal, in conformity with Pasteur's law of Molecular Dissymmetry.

2. The magnetic susceptibilities of the racemic modifications do not, in general, differ appreciably from those of the optically active and oppo-

site forms, hence no definite conclusion on the nature of the racemic form can be drawn from these measurements.

3. The effect of position isomerism on magnetic susceptibility has been studied and it is concluded that no definite rule is obeyed in regard to the sequence of magnetic susceptibility in position isomers.

4. The observed values (O) of gram molecular susceptibilities (χ_M) of camphor-β-sulphonates are generally less than the sum (C) of χ_m of their components. The camphor-β-sulphonates investigated fall into three groups according as O−C is negligible, nearly equal to $10{\cdot}5 \times 10^{-6}$ or varies from $26{\cdot}25 \times 10^{-6}$ to $34{\cdot}76 \times 10^{-6}$.

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CHROMONES

Part I. Nitration of Some 7-Hydroxychromones and Their Methyl Ethers

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No systematic study of the nitration of chromones appears to have been made so far, although a few nitrochromones have been prepared by direct nitration of some of the naturally occurring flavones like chrysin,[1] apigenin,[2] quercetin pentamethyl ether,[3] luteolin tetramethyl ether and morin pentamethyl ether.[4] Two other attempts at nitration of chromones are due to Simonis who succeeded in preparing 6-nitro-2: 3-dimethylchromone[5] and 6-nitro-2: 3: 5: 7-tetramethylchromone.[6] Bogert and Marcus[7] in their attempts to nitrate flavone failed to isolate any pure nitro-compound, a mixture of 2′-, 3′-, and 4′-nitroflavones being obtained.

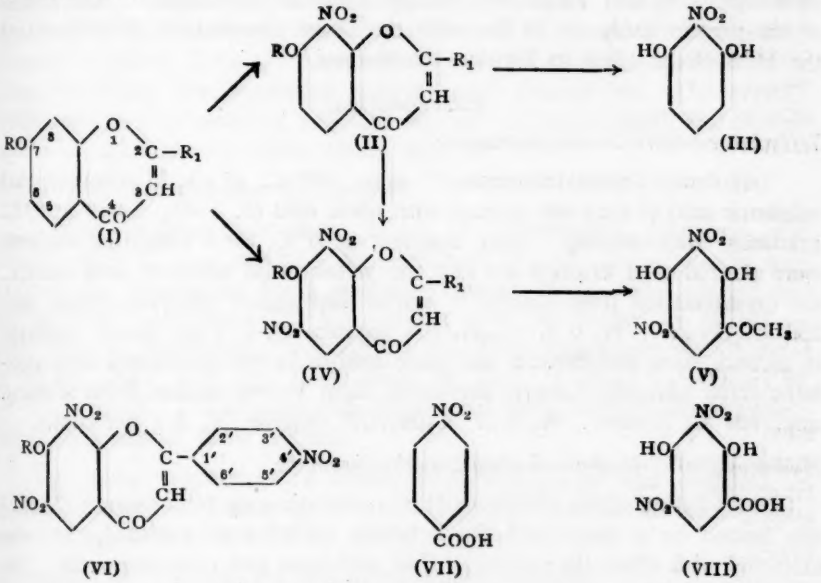
As a part of a comprehensive and systematic study on substitution in chromones, in the present investigation nitration of 7-hydroxy-2-methylchromone (I: $R = H$; $R_1 = CH_3$), 7-hydroxy flavone (I: $R = H$; $R_1 = Ph$) and their methyl ethers has been carried out under various conditions.

7-Hydroxy-2-methylchromone (I: $R = H$; $R_1 = CH_3$) at 0° C. with nitric acid (d. 1·42) in concentrated sulphuric acid gave a mono-nitro derivative which, on hydrolysis, yielded 2-nitro resorcinol (III) and was therefore 7-hydroxy-8-nitro-2-methylchromone (II: $R = H$; $R_1 = CH_3$). The methyl ether of I ($R = R_1 = CH_3$) also gave 8-nitro derivative as the product was identical with the methyl ether of the nitro-hydroxy compound. In the latter case, it may be pointed out that the usual methods of methylation, namely, with dimethyl sulphate and alkali in cold or with methyl iodide in presence of anhydrous potassium carbonate in acetone proved unsuccessful. Recourse was therefore taken to a method using dry sodium salt of the hydroxychromone with dimethyl sulphate in toluene, which gave good results with all the nitro-hydroxy compounds.

When the nitration of 7-hydroxy-2-methylchromone was carried out at room temperature (30° C.) using fuming nitric acid in concentrated sulphuric acid a di-nitro-product was obtained, which was also obtained on further nitration of the above mono-nitro-hydroxychromone. It was found to be 7-hydroxy-6: 8-dinitro-2-methylchromone (IV: $R = H$; $R_1 = CH_3$

as on alkaline degradation it furnished 3: 5-dinitroresacetophenone (V). It is interesting to note that while the 8-nitro compound underwent hydrolysis giving presumably a resorcylic acid derivative which on subsequent decarboxylation gave 2-nitroresorcinol, the 6: 8-dinitro-derivative, like 7-hydroxychromones,[8] gave the usual resacetophenone derivative. The methyl ether of the dinitro product (IV: R = R_1 = CH_3) was found to be identical with the dinitro product obtained by direct nitration of 7-methoxy-2-methylchromone.

All attempts to get higher nitro-derivatives proved unsuccessful, resulting in rupture of the pyrone ring. If nitration was attempted in acetic acid 3: 5-dinitro-β-resorcylic acid (VIII) was obtained, while in presence of sulphuric acid splitting took a different course giving 3: 5-dinitroresacetophenone (V).



The nitration of 7-hydroxyflavone (I; R = H; R_1 = Ph) took a similar course and furnished 8-nitro- and 6: 8-dinitro-7-hydroxyflavones (II: R = H; R_1 Ph and IV: R = H; R_1 = Ph respectively) as was shown by their degradation products which were identified as 2-nitroresorcinol (III) and 3: 5-dinitro resacetophenone (V) respectively. When heated on a steam-bath with concentrated nitric acid (d. 1·42) it also furnished a trinitro-derivative which on hydrolysis gave *p*-nitrobenzoic acid (VII), indicating

that further nitration has taken place in 4'-position. As the trinitro derivative could also be obtained by further nitration of 7-hydroxy-6: 8-dinitroflavone, the structure was assigned as 7-hydroxy-6: 8: 4'-trinitroflavone (VI). Attempts to further nitrate the compound only resulted in rupture of the γ-pyrone ring, *p*-nitrobenzoic being isolated. As before, the mono- and di-nitro-derivatives of 7-methoxy flavone (I: $R = CH_3$; $R_1 = Ph$) were found to be identical with the methyl ethers of the corresponding hydroxynitroflavones, showing that they underwent similar substitution.

The marked reactivity of the 8-position in 7-hydroxychromones has been observed before and is evident from the formation of the 8-aldehyde by the action of formylating agents on 7-hydroxy-3-methoxyflavone.[9] It is the 8-position which is involved in the Fries migration of 7-acetoxy-2-methylchromone[10] and in the Claisen transformation of the alkyl ethers of 7-hydroxyflavone and 7-hydroxy-2-methyl-3-methoxychromone.[11] The results of the present study are in line with the above observations demonstrating the Mills-Nixon effect in 7-hydroxychromones.[12]

Experimental

7-Hydroxy-8-nitro-2-methylchromone

7-Hydroxy-2-methylchromone,[13] m.p. 249° C. (1 g.) in concentrated sulphuric acid (5 c.c.) was treated with nitric acid (d. 1·42; 5 c.c.) at 0° C. gradually with stirring. After standing at 0° C. for 4 hours the contents were poured over crushed ice and the yellow solid collected and washed. On crystallisation from alcohol it yielded dark yellow rhombic plates, m.p. 268° C. (Found: N, 6·5. $C_{10}H_7O_5N$ requires N, 6·3 per cent.). Soluble in alcohol ether and benzene and gave reddish brown coloration with alcoholic ferric chloride. *Acetyl* derivative, light brown needles from alcohol, m.p. 164° C. (Found: N, 5·5. $C_{12}H_9O_6N$ requires N, 5·3 per cent.).

Hydrolysis of 7-Hydroxy-8-nitro-2-methylchromone

The solution of the chromone (1 g.) in caustic soda (4 per cent.; 25 c.c.) was heated on a steam-bath for 2 hours, cooled and acidified. It was extracted with ether, the extract washed and dried and ether removed. The oily residue with a smell resembling that of *o*-nitrophenol was crystallised from aqueous alcohol in orange prisms, m.p. 84° C. It did not depress the melting point of an authentic sample of 2-nitroresorcinol, m.p. 84° C., prepared by the method of Hodgson and Dyson.[14]

7-Methoxy-8-nitro-2-methylchromone

7-Methoxy-2-methylchromone[13] was prepared from 7-hydroxy-2-methylchromone (1 g.) by methylation with methyl iodide (5 g.) and potassium

carbonate in dry acetone (50 c.c.). The mixture was refluxed for 24 hours, acetone removed and diluted with water. The light brown solid was washed with dilute alkali and crystallised from dilute alcohol, white needles, m.p. 112° C. Kostanecki and Rozycki[13] give m.p. 113° C. It was dissolved in concentrated sulphuric acid (5 c.c.) and nitrated with nitric acid (d. 1·42; 5 c.c.) at 0° C. After keeping for two hours it was worked up as before when the nitro compound separated as white plates from alcohol, m.p. 211° C. (Found: N, 6·2. $C_{11}H_9O_5N$ requires N, 6·0 per cent.). It did not depress the melting point of the methyl ether of 7-hydroxy-8-nitro-2-methylchromone prepared as below.

7-Hydroxy-8-nitro-2-methylchromone (1·5 g.) was suspended in absolute alcohol (20 c.c.) and caustic soda solution (25 per cent.; 1 c.c.) added and stirred. After two hours in a refrigerator the orange-yellow sodium salt was collected, washed with absolute alcohol and dried at 120° C. for 4–5 hours. It (1 g.) was heated with dry toluene (15 c.c.) and freshly distilled dimethyl sulphate (5 c.c.) on an oil-bath at 120° C. for 4 hours. After steam-distillation the remaining solution was filtered hot. The crystals which separated on standing, collected washed with dilute alkali and crystallised from alcohol, tiny white plates, m.p. 211° C.

7-Hydroxy-6: 8-dinitro-2-methylchromone

7-Hydroxy-2-methylchromone (1 g.) in concentrated sulphuric acid (10 c.c.) at 0° C. was treated with nitric acid (d. 1·5; 5 c.c.) slowly with stirring, the temperature being maintained below 10° C. The mixture was left at room temperature (30° C.) and the next day worked up as before. After three crystallisations from alcohol the dinitro compound was obtained in yellow plates, m.p. 233° C. (Found: N, 10·3. $C_{10}H_6O_7N_2$ requires N, 10·5 per cent.). Dissolves in soda bicarb. and gives reddish brown coloration with alcoholic ferric chloride.

The same 7-hydroxy-6: 8-dinitro-2-methylchromone was obtained on further nitration of 7-hydroxy-8-nitrochromone with concentrated sulphuric and fuming nitric acid (d. 1·5; 5 c.c.) at 30° C.

Hydrolysis of 7-Hydroxy-6: 8-dinitro-2-methylchromone

The dinitrochromone (1 g.) was hydrolysed by heating its solution in caustic soda (4 per cent.; 20 c.c.) on a steam-bath for two hours. The light brown substance obtained on cooling and acidification, after three crystallisations from alcohol, gave pale yellow tiny crystals, m.p. 167° C. More of the same compound was obtained on extraction of the filtrate with ether. It did not depress the melting point of 3: 5-dinitroresacetophenone prepared as below.

3 : 5-Dinitroresacetophenone

3 : 5-Dinitroresacetophenone does not appear to have been prepared by direct nitration of resacetophenone. Adams[15] isolated it in an attempt to nitrate 4-O-acetylresacetophenone. In the present case it was prepared by direct nitration of resacetophenone as follows.

Resacetophenone (5 g.) was dissolved in acetic acid (20 c.c.) and nitric acid (d. 1·42; 15 c.c.) was slowly added. After the vigorous reaction subsided, it was heated on a steam-bath for 15 minutes and poured on crushed ice. 3 : 5-Dinitroresacetophenone that separated was crystallised from alcohol several times when yellow crystals, m.p. 167° C., were obtained. Adams [15] gives the same melting point.

7-Methoxy-6 : 8-dinitro-2-methylchromone

7-Methoxy-2-methylchromone was nitrated under identical conditions used for the dinitro of the hydroxychromone when 7-methoxy-6 : 8-dinitrochromone separated on diluting the reaction mixture with water. It was obtained first from hot water and then from alcohol in long rectangular plates, m.p. 114° C. (Found: N, 10·2. $C_{11}H_8O_7N_2$ requires N, 10·0 per cent.). It did not depress the melting point of the methyl ether of the dinitro-hydroxychromone prepared as below.

A solution of sodium hydroxide (25 per cent; 2 c.c.) was added to 7-hydroxy-6 : 8-dinitro-2-methylchromone (2 g.) suspended in alcohol (25·30 c.c.). On standing the yellow sodium salt separated which was collected and dried as before. The sodium salt (1 g.), dimethyl sulphate (5 c.c.) and toluene (15 c.c.) were refluxed on an oil-bath at 125° C. for 24 hours, and worked up as before. It crystallised from alcohol, white plates, m.p. 114° C.

Action of nitric acid on 7-Hydroxy-2-methylchromone at 100° C.

7-Hydroxy-2-methylchromone (1 g.) in acetic acid (10 c.c.) was heated with nitric acid (d. 1·42; 5 c.c.) on a water-bath for 4 hours and worked up as before when a nitro-acid, m.p. 205° C., was obtained which was identified as 3 : 5-dinitro-β-resorcylic acid.[16]

If however the experiment was repeated in concentrated sulphuric cid (10 c.c.) with concentrated nitric acid (d. 1·42; 5 c.c.) or fuming nitric acid (5 c.c.), the product was found to be 3 : 5-dinitroresacetophenone, m.p. 167° C.

Similar results were obtained on attempting to further nitrate 7-hydroxy-6 : 8-dinitro-2-methylchromone.

7-Hydroxy-8-nitroflavone

7-Hydroxyflavone,[17] m.p. 240° C. (1 g.) was added in very small amounts to a cooled mixture of concentrated sulphuric acid (5 c.c.) and nitric acid (d. 1·42; 5 c.c.) with stirring. After leaving at room temperature overnight, it was poured into ice-cold water, the solid collected and washed. It was boiled with little alcohol (10 c.c.), collected and crystallised from a mixture of pyridine and acetic acid, tiny crystals, m.p. 300° C. (approx.) (Found: N, 4·8. $C_{15}H_9O_5N$ requires N, 4·9 per cent.). Faint coloration with alcoholic ferric chloride. *Acetyl* derivative, light brown needles from acetic acid, m.p. 256°–57° C. (Found: N, 4·5. $C_{17}H_{11}O_6N$ requires N, 4·3 per cent.).

Hydrolysis of 7-Hydroxy-8-nitroflavone

The nitroflavone (1 g.) in caustic soda (4 per cent.; 25 c.c.) was refluxed for 3 hours. It was cooled and filtered and the filtrate shaken with ether. The residue after removal of ether was dissolved in water and steam-distilled. The distillate extracted with ether, the extract dried and ether removed. The residue was crystallised from alcohol (50%) when orange crystals of 2-nitroresorcinol m.p. 84° C. were obtained.

7-Methoxy-8-nitroflavone

7-Hydroxyflavone (1 g.), anhydrous potassium carbonate (10 g.) and methyl iodide (10 g.) in dry acetone (50 c.c.) were refluxed gently for 24 hours, acetone removed and diluted with water. After washing with caustic soda solution (2 per cent.), the methyl ether was crystallised thrice from alcohol, white needles, m.p. 110° C. Emilewiz and Kostanecki[18] and Turner and Robinson[19] give the same melting point. The methyl ether (1 g.) was added in small amounts to a cooled mixture of concentrated sulphuric acid and nitric acid and left overnight at room temperature. The crude product was boiled with dilute alcohol (50 per cent.; 10 c.c.) and crystallised from acetic acid, white needles, m.p. 300° C. (Found: N, 4·8. $C_{16}H_{11}O_5N$ requires N, 4·7 per cent.). It did not depress the melting point of the methyl ether of hydroxy nitroflavone prepared below.

The dry sodium salt of 7-hydroxy-8-nitroflavone (1 g.), prepared by treating the flavone in alcohol suspension with strong caustic soda solution, dimethyl sulphate (5 c.c.) and dry toluene (15 c.c.) were heated for 6 hours at 125° C. (oil-bath). It was worked up as before and the residue after steam distillation filtered and the solid boiled with caustic soda (2 per cent.) for 15 seconds, washed and crystallised from acetic acid, m.p. 300° C.

7-Hydroxy-6: 8-dinitroflavone

Nitric acid (d. 1·42; 5 c.c.) was added to 7-hydroxyflavone (1 g.) in acetic acid (7 c.c.) and heated on a steam-bath for 20 minutes. The light

yellow needles which separated were collected after cooling and washed with acetic acid, m.p. 288°–89° C. (Found: N, 8·8. $C_{15}H_8O_7N_2$ requires N, 8·5 per cent.).

7-Hydroxy-8-nitroflavone on further nitration with nitric acid in sulphuric acid yielded the same dinitroflavone, m.p. 288°–89° C.

On hydrolysis by refluxing with sodium hydroxide solution (10 per cent.) for about 3 hours yielded 3: 5-dinitro-resacetophenone, m.p. 167° C.

7-Methoxy-6: 8-dinitroflavone

7-Methoxyflavone (1 g.), acetic acid (7 c.c.) and nitric acid (d. 1·42; 5 c.c.) were heated on a steam-bath for 20 minutes and poured into ice-cold water. The product was washed and crystallised from alcohol, m.p. 221° C. (Found: N, 8·1. $C_{10}H_{10}O_7N_2$ requires N, 8·2 per cent.). It did not depress the melting point of the product obtained by methylation of 7-hydroxy-6: 8-dinitroflavone (below).

The sodium salt of 7-hydroxy-6: 8-dinitroflavone prepared as before (0·8 g.) was refluxed with toluene (10 c.c.) and dimethyl sulphate (5 c.c.) at 125° C. for 6 hours. It was worked up as before and the residue after steam distillation suspended in alcohol and caustic soda (few drops of 25 per cent.) added to convert the unreacted hydroxy compound into the sodium salt. The mixture was filtered and washed with cold alcohol. It was then boiled with water to remove the sodium salt, the solution filtered hot and the residue washed with hot water. On crystallisation from alcohol it furnished white needles, m.p. 222° C.

7-Hydroxy-6: 8: 4′-trinitroflavone

7-Hydroxyflavone (1 g.) was added to nitric acid (d. 1·42; 10 c.c.) and heated gently on a steam-bath until the vigorous evolution of the fumes subsided. After half an hour it was poured over crushed ice and the solid crystallised several times from acetic acid when pale yellow needles, m.p. 300°–05° C. were obtained (Found: N, 11·1. $C_{15}H_7O_9N_3$ requires N, 11·3 per cent.).

The trinitro derivative could also be prepared by treating 7-hydroxy-6: 8-dinitroflavone with nitric acid (d. 1·42; 10 c.c.) on a steam-bath for half an hour.

Hydrolysis of 7-Hydroxy-6: 8: 4′-trinitroflavone

The trinitroflavone (1 g.) was refluxed with sodium hydroxide solution (2 N.) for 4 hours. On cooling and acidification a yellow substance gradually separated. It was crystallised from acetic acid, tiny yellow needles, m.p.

237° C. It did not depress the melting point of an authentic specimen of para-nitrobenzoic acid. No other product could be isolated in a pure state.

Action of nitric acid on 7-hydroxyflavone on steam-bath

7-Hydroxyflavone (1 g.) in concentrated sulphuric acid (10 c.c.) and nitric acid (d. 1·42; 5 c.c.) were heated on a steam-bath for 4 hours and the reaction mixture worked up as usual when *p*-nitrobenzoic acid, m.p. 237° C., was obtained.

Summary

No systematic study of the nitration of chromones appears to have been carried out previously, though a few naturally occurring flavones have been nitrated. In the present work, nitration of 7-hydroxy-2-methylchromone and 7-hydroxyflavone and their methyl ethers has been studied. The mononitro-derivatives have been found to be 8-nitro compounds while the di-derivatives were 6:8-dinitro products. 7-Hydroxyflavone gave also a trinitro derivative which was found to be 7-hydroxy-6:8:4′-trinitroflavone. The constitutions of the nitro compounds were proved by alkaline hydrolysis.

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PRODUCTION OF THE *JOSHI-EFFECT* IN THE AERIAL CURRENT UNDER ELECTRICAL DISCHARGE IN CHLORINE

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Introduction

Production of the above phenomenon, an instantaneous and reversible photo-variation (usually though not invariably diminution, $-\Delta i$) of the conductivity, i especially of halogen under electrical excitation, has interest not only from the standpoint of discharge reactions but also as a partial analogue of Budde effect (Joshi,[1, 6, 8] 1943, 1945, 1947). The Budde effect refers to a small pressure rise, produced (photo-chemically) in chlorine and bromine in the absence of an external electrical field. Amongst points of contrast between these two effects the pronounced susceptibility of $-\Delta i$ to electrical factors is significant (Joshi,[1, 3] 1943). This last was observed markedly by the author in results for the effect $-\Delta i$ under uni- and bi-electrode excitation of the system (Prasad,[9] 1946). Subsequent studies of $-\Delta i$ in half and full-wave detection showed the importance of the nature of the detector on its meagnitude (Prasad,[10] 1947). It has now been observed *inter alia* with a given mode of excitation and detecting mechanism and in an *isolated* sample of pure chlorine, the effect $-\Delta i$ can be increased over a range of 5–90% current decrease under but ordinary light by a mere appropriate adjustment of associated factors.

Experimental

The general apparatus and the circuit employed are shown in Fig. 1. A Siemens' (glass) ozoniser was *uni-electrodically* excited in the range 4·8 to 9·6 kV (r.m.s.) of 50 cycle frequency. The ozoniser was filled with purified chlorine at the optimum gas pressure determined by preliminary trial experiments to be 300 mm. Hg. The observations of the current when the ozoniser was in dark, (i_D); and under light of a 200 watts incandescent (glass) bulb, (i_L), were made using a double diode RCA (6H6), on frame and single wire ærials; as also in the low tension line under the arrangements *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h* and *k* described later. Results for the net *Joshi-effect* denoted by $\Delta i = i_D \sim i_L$ and its relative value $\%\Delta i = 100 \times \Delta i/i_D$ are

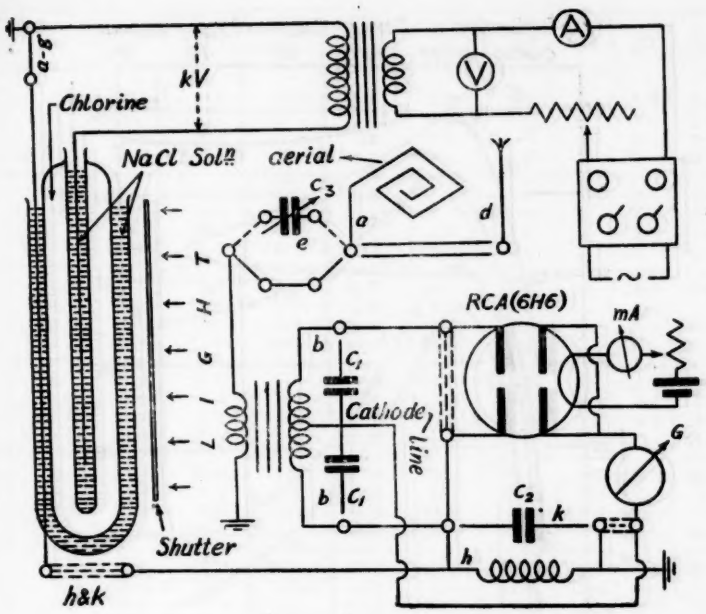

FIG. 1

returned in Table I under columns headed by *a*, *b*,.... *k*. For purposes of comparison, values for the relative effect $\%\Delta i$ under circuits *a* to *k* are expressed graphically in Fig. 2.

The two plates of the double diode were connected separately to the secondaries of a Bell transformer and the two cathodes together to the centre thereof, through a D.C. reflection galvanometer; the primary of the transformer was connected to a frame aerial in *a*. In series *b* and *c*, the above circuit (*i.e.*, in *a*) was modified by introducing two equal by-pass capacitances ($C_1 = 0{\cdot}0001\ \mu f$ in *b* and $C_1 = 0{\cdot}05\ \mu f$ in *c*) between the transformer secondaries and on either side of the *cathode-line* (see Fig. 1). Only one typical series of results for each is shown under columns *a*, *b* and *c* respectively in Table I. The variation of the corresponding $-\%\Delta i$ under the above arrangements is shown by the curves *a*, *b* and *c* respectively, in Fig. 2, as a function of applied potential, kV.

In the next series of experiments whose typical results are shown under *d* and *e* in Table I and by curves marked *d* and *e* in Fig. 2, the frame aerial in *a* was replaced by a single wire aerial, and a *serial* capacitance ($C_3 = 0{\cdot}05\ \mu f$)

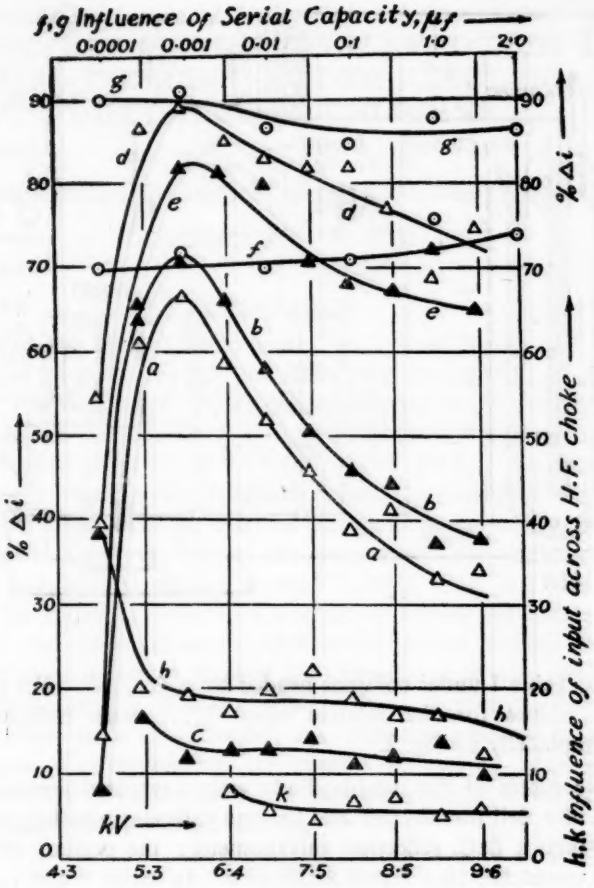

FIG. 2

was introduced in *e* only. In series *f* and *g*, the exciting potential was kept constant at 5·9 kV; the corresponding serial capacitance C_3 in *e* was varied in the range 0·0001–2·0 μf. This affected the frequency of the currents input to the detector. These results observed with frame and single wire aerials are shown under *f* and *g* in Table I; and graphically in respect of the corresponding $-\%\Delta i$ by curves *f* and *g* in Fig. 2, respectively.

The predominant role of the high frequencies as the chief seat of $-\Delta i$ (Joshi,[4] 1944) observed in aerial currents in the arrangements *a*, *b*,....*g*

TABLE I. *Influence of the detecting mechanism on* Joshi-effect *in chlorine*

Applied potential kV*	Discharge current (i)	Mode of detection									
		(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*h*)	(*k*)	(*f*)	(*g*)	
4·8	i_D	2·7	1·3	1·6	3·3	1·3	2·5	..	8·9	9·4	0·0001 μf
	i_L	2·3	1·2	..	1·5	0·8	1·5	..	2·7	0·9	
	Δi	0·4	0·1	..	1·8	0·5	1·0	..	6·2	8·5	
	$\%\Delta i$	14·8	7·7	..	54·5	38·5	40·0	..	70	90	
5·3	i_D	7·9	3·5	2·4	8·3	7·6	5·0	..	12·1	9·9	0·001 μf
	i_L	3·1	1·2	2·0	1·0	2·7	4·0	..	3·4	0·9	
	Δi	4·8	2·3	0·4	7·3	4·9	1·0	..	8·7	9·0	
	$\%\Delta i$	60·8	65·7	16·7	87·9	64·5	20·0	..	72	91	
5·9	i_D	17·8	6·7	3·3	16·0	10·0	8·0	..	13·3	10·2	0·01 μf
	i_L	5·9	1·9	2·9	1·8	1·8	6·5	..	4·0	1·3	
	Δi	11·9	4·8	0·4	14·2	8·2	1·5	..	9·3	8·9	
	$\%\Delta i$	66·9	71·6	12·1	88·8	82·0	18·8	..	70	87	
6·4	i_D	23·9	9·3	3·9	19·3	12·3	11·5	6·5	12·6	10·5	0·1 μf
	i_L	9·9	3·2	3·4	2·8	2·3	9·5	6·0	3·7	1·6	
	Δi	14·0	6·1	0·5	16·5	10·0	2·0	0·5	8·9	8·9	
	$\%\Delta i$	58·6	65·6	12·8	85·5	81·3	17·4	7·7	71	85	
6·9	i_D	30·7	11·8	5·2	21·7	13·5	15·0	9·0	13·7	10·8	1·0 μf
	i_L	14·9	4·9	4·5	3·7	2·7	12·0	8·5	3·3	1·3	
	Δi	15·8	6·9	0·7	18·0	10·8	3·0	0·5	10·4	9·5	
	$\%\Delta i$	51·5	58·5	13·5	82·9	80·0	20·0	5·5	76	88	
7·5	i_D	38·9	15·3	5·7	25·0	13·3	20·0	11·5	13·5	11·3	2·0 μf
	i_L	20·9	7·7	4·9	4·5	3·9	15·5	11·0	3·5	1·5	
	Δi	18·0	7·6	0·8	20·5	9·4	4·5	0·5	10·0	9·8	
	$\%\Delta i$	46·3	49·7	14·0	82·0	70·7	22·5	4·3	74	87	
8·0	i_D	45·7	19·3	7·9	26·7	16·4	24·0	15·0			
	i_L	27·7	10·5	7·0	4·7	5·2	19·5	14·0			
	Δi	18·0	8·8	0·9	22·0	11·2	4·5	1·0			
	$\%\Delta i$	39·4	45·6	11·4	82·4	68·3	18·8	6·7			
8·5	i_D	60·0	25·0	9·5	30·5	18·5	29·0	18·0			
	i_L	35·0	14·0	8·4	7·0	6·0	24·0	16·5			
	Δi	25·0	11·0	1·1	23·5	12·5	5·0	1·5			
	$\%\Delta i$	41·7	44·0	11·6	77·1	67·6	17·2	8·3			
9·1	i_D	69·8	32·0	11·7	26·5	21·5	35·0	22·0			
	i_L	46·8	20·0	10·1	8·2	6·0	29·0	21·0			
	Δi	23·0	12·0	1·6	18·3	15·5	6·0	1·0			
	$\%\Delta i$	32·9	37·5	13·7	69·1	72·1	17·1	4·5			
9·6	i_D	84·2	41·2	14·7	27·5	27·1	40·5	26·5			
	i_L	55·7	25·5	13·2	7·0	9·6	35·5	25·0			
	Δi	28·5	15·7	1·5	20·5	17·5	5·0	1·5			
	$\%\Delta i$	33·9	38·1	10·2	74·5	64·6	12·3	5·7			

* Varied only in *a*, *b*, *c*, *d*, *e*, *h* and *k*.

Currents observed in aerials at variable kV.

(*a*) Frame aerial, full-wave detection.
(*b*) With 0·0001 μ*f* on either side of cathode-line in (*a*).
(*c*) Capacity in (*b*) changed to 0·05 μ*f*.
(*d*) Single wire aerial, full-wave detection.
(*e*) 0·0001 μ*f* added in (*d*).

Currents observed at constant kV and capacities in series with the aerial.

(*f*) Same as (*a*) but with 0·0001–2·0 μ*f*.
(*g*) Same as (*b*) " " "

Currents observed in L. T. line, at variable kV.

(*h*) H. F. choke, half-wave detection.
(*k*) Same as (*h*) but with a parallel 0·05 μ*f*.

described above is revealed markedly by values for the effect $-\Delta i$ measured in the low tension line of the excited system; the detector double diode was coupled with the L.T. line of the ozoniser circuit by means of an air cored high frequency choke coil. To one end of this last, two plates of the diode were connected together; its other end was earthed; as also the cathodes (connected together) through the galvanometer (Fig. 1 *h* and *k*). In series of experiments whose typical observations are shown by curve *k* (Fig. 2) and under column *k* in Table I, a by-pass condenser ($C_2 = 0{\cdot}05\,\mu f$) was connected across the high frequency choke coil.

Discussion

It has been established (Joshi,[2, 6, 7] 1929, 1945, 1946) that below V_m, the threshold potential, which is determined by a number of factors such as temperature, gas pressure and especially the frequency of excitation, the effect $-\Delta i$ is negligibly small; and that *numerically* it attains to a maximum near V_m. The threshold potential V_m may be identifiable with, or a simple function of the Paschen or spark potential especially in elementary gases (Joshi,[5] 1944). It is significant that despite the wide variation in the modes of current detection (*a*, *b*,....*k*), the threshold potential is constant, *viz.*, 4·3 kV. The quantity V_m and its neighbourhood imply therefore, a critical region for the production of the effect $-\Delta i$. With the exception of results in the two series referred to by *f* and *g* in Table I and Fig. 2, in which the applied potential was not varied, in every one of the arrangements *a*, *b*,....*k*, it is observed that numerically the maximum $-\%\Delta i$ occurs near V_m, *viz.*, within 5·3–5·9 kV and decreases progressively thereafter. It may be emphasised at this stage that the aerial current was unobserved within the limitations of the available detector, at exciting potentials less than the threshold potential V_m. This represents an extension of a general finding due to Joshi[6] (1945).

It is instructive to observe that for a given difference in the applied kV, percentage increase in i_D and $-\Delta i$ and relative variation in $-\%\Delta i$ are more rapid near V_m than above it. Thus, *e.g.*, in diode detection on changing the potential from 4·8 to 5·3 kV, whilst i_D and $-\Delta i$ increase from 2·7 to 7·9, and 0·4 to 4·8 respectively, the corresponding $-\%\Delta i$ rises from 14·8 to 60·8. When, however, the applied kV rises from 9·1 to 9·6, i_D and $-\Delta i$ increase from 69·8 to 84·2 and 23·0 to 28·5 respectively; the corresponding $-\%\Delta i$ remains, however, practically constant at 33. This is explicable on the following consideration: At the threshold potential, the gas breaks down as a dielectric, and the effect $-\Delta i$ sets in (Joshi,[6] 1945). With a further increase of the applied kV, the system develops a stabler regime

appropriate under the enhanced excitation. Thus, a rapid change of i_D, $-\Delta i$, and $-\%\Delta i$ near V_m as against those at the higher kV, when the discharge is comparatively stabler, as observed is to be anticipated.

That the discharge current consists of several frequency bands ranging from the supply frequency to radio regions; and that preferentially, the effect $-\Delta i$ develops in the high frequency part of the conductivity has been generalised by Joshi[3, 4] (1943, 1944). At greater kV as is to be anticipated, not only i_D but also the net effect $-\Delta i$ are observed to be larger; the corresponding relative effect $-\%\Delta i$ is, however, disproportionately low, as a general characteristic result. This suggests that with increase of kV, an initial increase of the H.F. component anticipated on general consideration is followed by its decrease; or else, that the proportion of the L.F. or/and medium frequencies preponderates in the overall conductivity under the discharge. Results in Fig. 1 and Table I show that the arrangements *b* and *c* are comparatively capacitative by-passing circuits; and that therefore, as is to be expected, *ceteris paribus*, i_D and $-\Delta i$ decrease in the order $a > b > c$. Thus, *e.g.*, at 5·9 kV, i_D and $-\Delta i$ respectively in *a*, *b* and *c* are (17·8, 11·9), (6·7, 4·8) and (3·3, 0·4). This decrease of i_D and $-\Delta i$ in *b* and *c* is attributable to the capacitative by-passing of the H.F.'s, which represent predominantly the seat of $-\Delta i$. The arrangements *b* and *c* should show smaller $-\%\Delta i$. At the special value of the capacity $= 0{\cdot}0001\,\mu f$, the $-\%\Delta i$ is surprisingly high, *viz.*, a 70% current decrease at 5·9 kV. This (apparent) deviation as also the entire series of results under *a*, *b* and *c* were reproducible within 1% when the observations were repeated five times; further work has shown that a tuning effect is in part responsible for the above result.

It is remarkable to see from Table I that $-\Delta i$ and $-\%\Delta i$ in single wire aerial reception is larger as compared to frame aerial despite the markedly low i_D in the former. Thus, *e.g.*, at 5·9 kV, the ratios of $-\Delta i$ and $-\%\Delta i$ in single wire aerial to frame aerial are 14·2 : 11·9 and 88·8 : 66·9 respectively. As suggested by Joshi[5] (1944) this may be ascribed to the small aerial capacity and therefore, to a comparatively higher frequency input to the detector. This deduction is in accord with the results obtained in the relative study of the arrangements *d* and *e*, *i.e.*, in single wire aerial reception and with a serially introduced capacity. Due to the addition of the latter at $C_3 = 0{\cdot}0001\,\mu f$, $-\%\Delta i$ thus decreased from 88·8 to 82·0 at 5·9 kV. Influence of an increase in serial capacity at constant kV both in frame as well as in single wire aerials is to increase i_D and (numerically) $-\Delta i$.

A further illustration of the influence of frequency component in the determination of Δi, is shown by the results obtained under the arrangements

h and *k*; these circuits include for the coupling inductance in the L.T. line and for the by-pass condenser respectively, a high frequency choke coil and a $0{\cdot}05\,\mu f$. Due to the former only high frequency currents would be admitted to the detector; besides, the latter would filter out an appreciable part of these H.F.'s. The decrease of i_D, $-\Delta i$ and $-\%\Delta i$ in *k* as observed follows from considerations mentioned above.

As a further illustration of the important role of the electrical factors in altering not only the magnitude *but even the sign of the effect* $-\Delta i$, it may be mentioned that in diode detection as employed above with by-pass capacities exceeding $0{\cdot}05\,\mu f$ a *positive Joshi-effect* $+\Delta i$, *viz* +., a photo-increase of *i* was producible *ad lib* over a wide range of exciting kV. Thus, *e.g.*, using $0{\cdot}05\,\mu f$ as by-pass capacities at 5·3 kV, $+\%\Delta i$ was 48·0 which decreased with increase of kV and also with the magnitude, of the by-pass capacities. Repeated observations showed that in aerial current under the arrangement *c* which is essentially similar to that mentioned above, no positive effect was produced at any stage. It is concluded therefore, that comparatively low or medium frequency currents as distinct from those of H.F.'s observed in the aerial current may be associated with the production of the *positive* effect.

In a recent theory of this phenomenon, Joshi[8] (1947) has postulated a boundary layer of ions and excited molecules formed under the discharge. As determined by the characteristic work function thereof, irradiation releases electrons (and less frequently) positive ions; former produce $-\Delta i$, due to negative ion formation, as a space charge effect. The positive ions lead to $+\Delta i$. The author's tentative suggestion that the positive *Joshi-effect* $+\Delta i$ is favoured by the medium and low frequencies (as distinct from the H.F. associated chiefly with $-\Delta i$) follows from a consideration of the relevant mass and velocity.

The pressure rise under the Budde effect in, *e.g.*, chlorine originates chiefly from a primary atomisation of the irradiated gas. The marked diversity of results illustrated by the positive and negative *Joshi-effect*; and particularly the profound influence thereon of the electrical parameters are to be expected from the behaviour of a much greater variety of particles, *viz.*, the positive, negative ions and electrons; as also of particles at various stages of excitation, produced under fields chracteristic of the discharge conditions.

Grateful thanks of the author are due to Prof. S. S. Joshi, D.Sc. (Lond.), F.R.I.C., F.A.Sc., for kind interest and valuable guidance during the work.

Summary

Arising out of Joshi's observation of the dependance of the *Joshi-effect* $-\Delta i$ on circuital parameters and especially the author's earlier work on Δi under uni- and bi-electrode excitation has been the finding that in an *isolated* sample of purified chlorine (300 mm.) excited by an ozoniser discharge due to 4–10 kV of 50 cycle frequency the negative *Joshi-effect* $\% \Delta i = 100 \times \Delta i/i_D$, detected with an aerial increased from 5–90% current diminution in but ordinary light, as its capacity was decreased progressively. Introduction of a serial capacitance in the aerial circuit tends to increase (numerically) the net *Joshi-effect* $-\Delta i$; that of a by-pass capacity decreases it. These results are in accord with Joshi's view that H.F.'s constitute the seat of $-\Delta i$. A large (48%) and reproducible *ad libitum* positive *Joshi-effect, i.e.*, an increase $+\Delta i$ of the discharge current under light, occurs in the L.T. line, especially under H.F. rejection, it is suggested that the positive effect may be associated with the *low* frequencies of the discharge current.

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VERTICAL DISTRIBUTION OF ATMOSPHERIC OZONE IN LOW LATITUDES

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§1. Introduction

The first rough estimates of the height of atmospheric ozone were obtained in 1925–27 from photometric measurements[1] of the spectrum of direct sunlight at different altitudes of the sun, and these gave a mean height of about 40-50 km. In 1929, F.W.P. Götz[2] observed that the light scattered from the zenith sky was relatively richer in ultraviolet light in the region of ozone absorption when the sun was on the horizon than when it was a few degrees higher up in the sky. He called this the ' Umkehr Effect ' and suggested that it could be used to deduce the vertical distribution of ozone in the atmosphere by taking observations of the light scattered from the blue zenith sky. Using the photo-electric spectrophotometer developed by Dobson,[3] Götz, Meetham and Dobson[4] made reliable measurements of the Umkehr Effect in 1934 at Arosa (Lat. 47° N.) in Switzerland and developed methods for calculating the vertical distribution of ozone. From 46 days' observations of the Umkehr curves in different seasons of the year and with different total amounts of ozone, they found that the average height of ozone at Arosa was about 22 km. above sea-level, that the ozone was distributed mainly between the ground and 35 km., and that the nature of the vertical distribution changed more or less systematically with the total amount of ozone, higher ozone amounts in general lowering the centre of gravity. The average height of ozone deduced from observations of zenith sky intensities was confirmed by Regener[5] from his independent studies of the ultraviolet end of the solar spectrum with spectrographs carried in sounding balloons.

The vertical distribution of atmospheric ozone in high latitudes was investigated by Meetham and Dobson[6] from observations made at Tromsø (Lat. 69° 40′ N.) in Norway in the summer of 1934. They could get only 13 days' observations. The average height of ozone was found to be slightly lower (20·8 km.) at the higher latitude, the maximum concentration of ozone also being in a region centred at 21 km.

Recently, Tønsberg and Langlo[7] have published a detailed account of their investigations on atmospheric ozone at Nordlysobservatoriet, Tromsø. These include measurements of the total quantity of ozone by sunlight,

starlight, and moonlight with different types of instruments during the years 1935–42. The zenith sky measurements for the vertical distribution of ozone were made with Dobson's photo-electric spectrophotometer during 1939–42. The measurements were more numerous than the observations made by Meetham and Dobson in 1934. The new Tromsø results show a markedly different type of distribution from the earlier results of Meetham and Dobson, the centre of gravity of ozone showing a variation from 26·7 km. for 0·160 cm. of ozone to 20·8 km. for 0·400 cm. in the new series as compared with a more or less fixed height of 20·8 km. in the old one. The new distributions show that, when the total amount of ozone varies, the most marked changes in the ozone content occur between 5 and 20 km.

§2. Observations in India

Little information has been available so far about the vertical distribution of atmospheric ozone in low latitudes. Observations with one of Dobson's photo-electric spectrophotometers were started in India at Poona (Lat. 18° 31′ N.) in February 1940 by Dr. Ramanathan and Umkehr curves for about six clear days were obtained during the months of February and March of that year. The fact that in low latitudes the height of the sun changes rapidly when it is near the horizon makes it rather difficult to take accurate and numerous observations at sunset or sunrise; still, the observations were good enough to indicate the existence of the 'Umkehr Effect'. The same instrument was later taken to Delhi (Lat. 28° 35′ N.) and systematic observations were made during the period November 1945 to March 1947. The calibration of the optical wedges in the instrument was in doubt and many clear days were spent in recalibrating the wedges. The new calibration[8] brought out some significant differences and these were taken into account in working out the results. Observations on many cloudless days in summer had to be excluded because of the peculiar white haze characteristic of the hot season in north-west India. About 35 clear days' Umkehr curves were obtained at Delhi. In April 1947, the same instrument was taken to Simla (31° 06′ N., 2·45 km. above sea-level) to clarify some points raised by the Delhi observations on the effect of dust and haze on the intensities of direct sunlight and zenith sky light. At Simla, 15 Umkehr curves were obtained in April and May 1947 and 9 curves in November 1947. The instrument was again taken to Poona and used during the months of February and March 1948, and Umkehr curves were obtained on eight clear days.

The present paper gives the results of the analysis of the zenith sky observations at Delhi and Poona. It was found that for the same quantity

of ozone (0·220 cm.), the average height of ozone at the latitude of Delhi is higher (25·1 km.) than the height 22·5 km. at Arosa.[4] At Tromsø, Meetham and Dobson's[6] analysis indicated a mean height of about 20·8 km. for this amount of ozone, while Tønsberg and Langlo[7] found it to be 25·7 km. The Umkehr curves and the average heights deduced from observations at Simla are more or less similar to those obtained at Delhi. At Poona, zenith sky observations are not available for the ozone amount 0·220 cm., but on a number of days when the ozone amount was between 0·164 and 0·177 cm., the average height was found to be about 28 km. Further work is required at Poona and still lower latitudes.

§3. Methods of Calculating the Vertical Distribution of Ozone

Two methods (A and B) for calculating the vertical distribution of ozone, which differ from each other only in matters of detail, have been described by Götz, Meetham and Dobson in their Arosa paper.[4] Observations are made on the light scattered from the clear zenith sky at different zenith distances Z of the sun. If I, I′, I″ be the intensities of the zenith-scattered light at the three wavelengths λ 3110 A, λ' 3300 A and λ'' 4450 A, the instrument directly gives log I/I′ + C and log I″/I′ + C′, where C and C′ are instrumental constants which are eliminated in the final calculations. When log I/I′ (C being dropped hereafter for convenience) is plotted against Z^4 (the fourth power being chosen to open out the scale at low altitudes of the sun), it is seen that log I/I′ continuously decreases with increasing values of Z, reaches a minimum when Z is 85° to 87° and again increases with further increase of Z. The shape of this curve, called 'Umkehr curve' by Götz, and the position of the inversion depend upon the height distribution of atmospheric ozone.

Considering the scattering by an element at height h above the earth's surface, the intensity I of light of wavelength λ reaching the instrument from unit angle of the zenith sky can be shown to be given by

$$I = K(1+\cos^2 Z) I_0 \int_0^\infty \rho_h \left[10^{-\alpha \int_h^\infty x_h \sec \xi_h \, dh - \alpha \int_0^h x_h dh} \times 10^{-\int_h^\infty \beta_h \sec \xi_h dh - \int_0^h \beta_h dh}\right] dh$$

$$= K(1+\cos^2 Z) I_0 \int_0^\infty \rho_h \cdot 10^{-\alpha V} \cdot 10^{-\beta F} \, dh.$$

Here,

$K = \frac{3}{16\pi} \cdot \frac{\beta}{H\rho_0}$ and is a constant proportional to the scattering per unit solid angle by unit volume of air, β being the scattering for the whole of the

atmosphere of homogeneous height H, and ρ_0 the density of air at the earth's surface,

Z = the zenith angle of the sun as seen from the earth's surface, *i.e.*, the angle between the incident sunlight and the scattered vertical ray,

ξ_h = the zenith angle of the sun as seen from a point in the atmosphere at height h from the earth's surface, *i.e.*, the angle between the incident sunlight and the normal to the shell of the atmosphere at height h,

I_0 = the intensity of the incident solar radiation of wavelength λ outside the earth's atmosphere,

ρ_h = density of the air at height h,

$\beta_h = \frac{\beta}{H\rho_0}\rho_h$ and refers to the scattering by air at height h,

α = the decimal absorption coefficient per cm. at N.T.P. of ozone at the wavelength λ,

x_h = the ozone amount per unit length at height h.

Y thus denotes the total integrated thickness of ozone traversed by sunlight from outside the atmosphere to the scattering element and afterwards by the scattered light from the latter on its way to the observing instrument. Y will therefore depend on the vertical distribution of ozone in the atmosphere. Similarly F denotes the integrated 'airmass' traversed, the integration being taken in a way similar to that for Y.

An expression similar to I can be written for the intensity I′ of the light of wavelength λ'. Hence Log I/I′ can be calculated and equated to the observed value. A strict mathematical solution for a given 'Umkehr curve' is not practicable and two different approximate methods have been given by Götz, Meetham and Dobson.

(*a*) *Method A.*—In this method, the atmosphere is divided into 5 sections, *viz.*, 0–5 km., 5–20 km., 20–35 km., 35–50 km. and above 50 km. The atmosphere above 50 km. is assumed to contain no ozone. In the lowest layer, the ozone amount is assumed to be what is given by spectroscopic or chemical measurements made at ground level. Let this be u cm. and let the unknown ozone amounts in the sections 35–50 and 20–35 km. be x_1 and x_2 respectively; then the ozone amount in the layer 5–20 km. is $x-(x_1+x_2+u)$, where x is the total ozone obtained from direct sun observations. The ozone in each section is assumed to be distributed uniformly. The two unknowns x_1 and x_2 can be determined by taking two suitable values of log I/I′ corresponding to two values of the zenith distance Z from an

observed mean Umkehr curve and writing down two numerical equations. Generally, log I/I′ corresponding to a third value of Z is used as a check. This method has been used by Tønsberg and Langlo in working out the ozone distribution at Tromsø from the observations during 1939–42.

(*b*) *Method B.*—Here, the whole atmosphere is divided into 8 sections and arbitrary amounts of ozone are assumed to be present in each, the sum of the amounts in all the sections together being equal to the total ozone amount. By calculating the scattering and absorption of light at all heights under these conditions, a theoretical 'Umkehr curve' can be calculated. This will, in general, differ from the observed curve and the assumed distribution of ozone in the various sections can be varied by trial and error until a reasonably good agreement is obtained between the calculated and observed curves. In general, more than one such solution can be found for a given Umkehr curve, but it is found that the solutions are not substantially different and the average height of ozone for all these is found to be almost identical. This method has been used by Götz, Meetham and Dobson in working out the ozone distributions from observations at Arosa and from the earlier series at Tromsø.

Method A was used for analysing the Indian data preliminarily in an exploratory manner so as to give an approximate idea of the ozone distributions. Method B was then applied on the basis of the results of method A, and the necessary variations in the assumed ozone quantities made so as to get a good fit with the observed Umkehr curves. Details of method B only are given below.

§4. Details of Method B used in India

In this method, Dobson divided the atmosphere into a number of horizontal sections such that the mass of air in any section was $1/\sqrt{10}$ of that in the section next below it. The whole of the air in any section is then supposed to be concentrated at such a height that half the air in the section is above that level and half below it. The ozone in each section is also supposed to be distributed in the same way as the air, which means that, within each layer, ozone is not uniformly distributed but decreases nearly exponentially with height.

Dividing the atmosphere in geometrical progression with a factor of $1/\sqrt{10}$ simplifies some numerical calculations. The method used in this paper is slightly different. The atmosphere is divided into layers each of 9 km. thickness from the sea-level upward. For simplicity in calculations, it was assumed that the centre of mass of each layer was situated at 3 km. above the base of that layer. This is usually correct to within ½ km., and

the approximation is good enough. For pressures, temperatures and densities upto 25 km. in the atmosphere, the average values given by Dr. Ramanathan[9] for Agra have been used; for 30 km. and upward, values recently given by Penndorf[10] are used. Table I below summarises the assumed values of temperatures, pressures and densities at different heights. Table II gives the heights of the different sections and the masses of air in the subsections.

TABLE I

Height a.s.l. km.	Temp. °A	Pressure mb.	Density gm./m³	Height a.s.l. km.	Temp. °A	Pressure mb.	Density gm./m³
0	300	1013·3	1176·7	30	227·5	11·7	17·9
2	288	799	966·6	35	233	5·56	8·31
5	270	554	714·9	40	263	2·79	3·70
10	239	284	414·0	45	293	1·55	1·84
12	225	210	325·2	50	323	0·86	0·93
15	206	130	219·9	60	283	0·28	0·35
17	199	93	162·8	70	243	0·076	0·11
20	208	56	93·8	80	203	0·017	0·029
25	217	26	41·1	90	275·5	0·0039	0·005
				100	348	0·0013	0·0013

TABLE II

Section No.	Boundaries of section: km.	Assumed C.G. of section:km.	Sub-section	Boundaries of sub-section:km.	Fraction of atmosphere in the sub-section
1	0–9	3	1*a*	0–3	·3022
			1*b*	3–9	·3776
2	9–18	12	2*a*	9–12	·1130
			2*b*	12–18	·1298
3	18–27	21	3*a*	18–21	·0302
			3*b*	21–27	·0288
4	27–36	30	4*a*	27–30	·00693
			4*b*	30–36	·00677
5	36–45	39	5*a*	36–39	·00162
			5*b*	39–45	·00163
6	45–54	48	6*a*	45–48	·000455
			6*b*	48–54	·000532
7	54–63	57	7*a*	54–57	·000155
			7*b*	57–63	·000200
8	63–72	66	8*a*	63–66	·000061
			8*b*	66–72	·000071

Scattering from all significant layers was taken into account when the sun was very near the horizon; with higher altitudes of the sun, the effect of the higher layers became less and less important.

All the ozone was assumed to be present only in the first six sections, *i.e.*, up to 54 km. The ozone in each section was further assumed to be uniformly distributed within each section, so that in considering the absorption due to ozone, two-thirds of the quantity in the section came in the slant path of the sunlight and only one-third in the lower vertical path.

To get the integrated 'airmass' F traversed by the sunlight along the slant path and by the scattered ray along the vertical path, F can be conveniently expressed in the form

$$F = \frac{\rho_h}{\rho_0} [f(Z) - 1] + 1$$

where $f(Z)$ is a function of Z. $f(Z)$ tends to sec Z for high altitudes of the sun; but owing to the curvature of the earth, $f(Z)$ differs increasingly from sec Z as Z approaches 90°. Götz[11] has given tables of slant length in different 2 km. steps above the point of observation for values of Z = 60°·75, 80°, 86°·5 and 90°. Similar tables were prepared for a few more angles and these were used in the calculations.

The following Table III gives the values of the scattering and absorption coefficients used in the calculations.

TABLE III

Wavelength	Decimal absorption coefficient per cm. of ozone at N.T.P.	Decimal scattering coefficient for the air in the whole atmosphere
λ 3110 A	α 1·275	β 0·457
λ' 3300 A	α' 0·074	β' 0·361
λ'' 4450 A	α'' 0	β'' 0·109

The scattering coefficients in the last column correspond to pure molecular scattering including anisotropic scattering and refer to the whole atmosphere above mean sea-level. The actual height of Delhi is 218 m. above sea-level and that of Poona is 563 m. and the assumption of pure molecular scattering is also not quite true even on apparently clear days. But considering the uncertainty of the amount of dust in the atmosphere above Delhi and Poona even on clear days and the fact that the errors caused by the above two discrepancies are of opposite signs, it was considered that the values adopted were good enough.

§5. Observational Data

Plotting log I/I′ against Z^4, Dobson found that for any group of days on which the total ozone content was nearly identical, the points lay practically on the same Umkehr curve. There was a largish scatter of points when Z was large and this was attributed to the larger errors of observation with weaker light. He concluded that the shape of the Umkehr curve and hence the vertical distribution of ozone was a function mainly of the total ozone content.

As regards the observational data at Delhi, the ozone amounts for which Umkehr curves were obtained during the period November 1945 to March 1947 varied only between 0·155 cm. and 0·217 cm., 35 good days' curves being obtained in all. Out of these, 27 curves were obtained during the period November to June. Dust and haze during the latter part of the hot season and cloudiness during the monsoon season make it difficult to obtain good observations during these seasons. The following table gives the number of Umkehr curves obtained for various amounts of ozone at Delhi.

Ozone amount	No. of Umkehr curves
<0·160 cm.	4
0·160—0·170 cm.	12
0·170—0·190 cm.	12
0·190—0·200 cm.	4
>0·200 cm.	3

For the purposes of calculations in this paper, a few representative curves relating to clear days will be taken and these are shown in Fig. 1. They relate to ozone amounts 0·155 cm. (lowest quantity observed on 6–1–46 at Delhi), 0·217 cm. (highest quantity observed on 20–1–47), 0·175 cm. (mean ozone amount for a group of 3 similar curves) and 0·200 cm. (the amount on another selected clear day). All these curves happen to be from the winter season and have a more or less uniform spread of ozone amounts and consistent changes in positions of inversion.

As regards the observational data at Poona, the curves relate to the period February and March 1948 only,* 8 good curves being obtained in

* There are a few days' observations taken by Dr. Ramanathan in 1940 when the instrument was first set up at Poona. The calibration of the optical wedges in the instrument was, however, not checked in 1940, and on doing this later in 1945 at Delhi, the new calibration showed some significant differences from the one supplied by the manufacturers. The calibration was therefore checked regularly on different occasions during the periods of observation at Delhi and Poona and fortunately it has been found to remain the same. Moreover, in 1940, zenith sky observations for values of the zenith distance Z of the

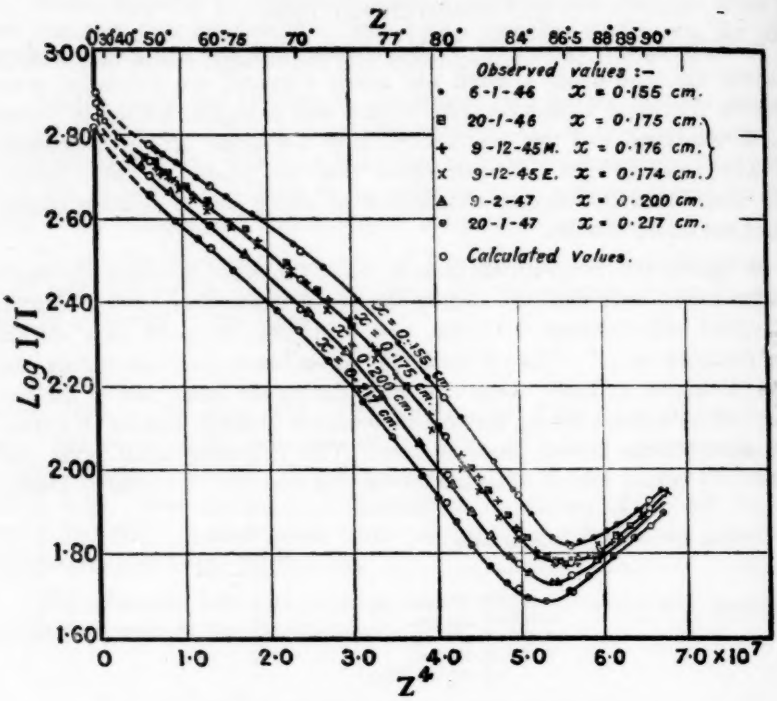

FIG. 1. Intensity of zenith sky light with different ozone amounts at Delhi

all for ozone amounts varying between 0·164 cm. and 0·177 cm. Fig. 2 gives two representative curves for Poona with ozone amounts 0·164 cm. and 0·174 cm.

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sun larger than 87° or 88° could never be obtained. The observations made in 1948 were quite satisfactory even upto Z = 90° or more, due to the increased sensitivity of the instrument resulting from the replacement of the old valves in the amplifier by new ones and also due to the use of higher voltages (within the limits allowed) for the amplifier and photo-cell when the incident light was weak at the time of sunrise or sunset. More weight has therefore to be given to the observations obtained in 1948.

Assuming the new calibration to hold good for the observations obtained in 1940, calculations were also made for an Umkehr curve with an average quantity 0·183 cm. of ozone and this gave about 30 km. as the average height of ozone over Poona. This may be compared with the average height 28·0 km. obtained in 1948 for an ozone amount 0·174 cm.

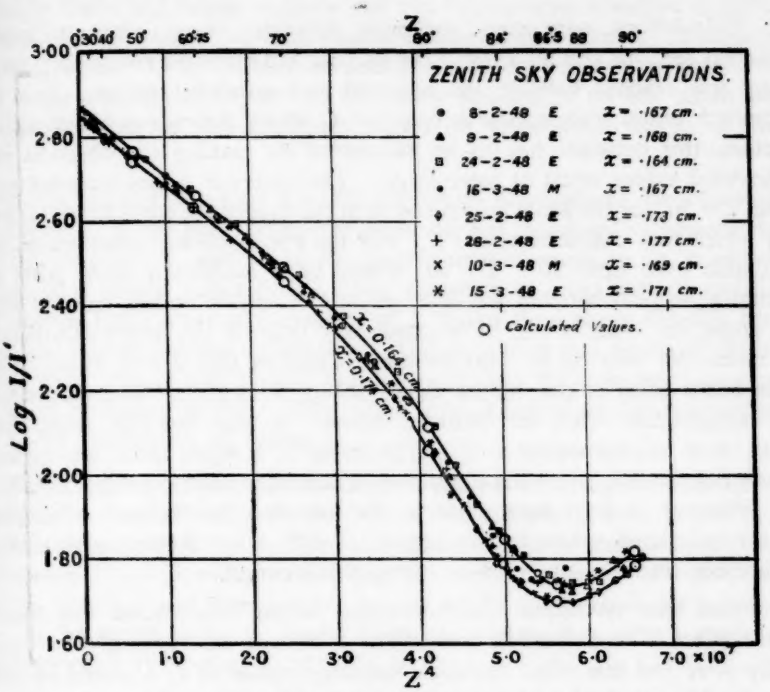

FIG. 2. Intensity of zenith sky light with different ozone amounts at Poona

§6. CALCULATION OF THE HEIGHT DISTRIBUTION AND RESULTS

Table IV shows the values of log I/I′ for the four curves relating to Delhi and the two curves relating to Poona for different zenith distances Z of the sun.

TABLE IV

Observed values of log I/I′ for different values of Z

Z	$Z^4 \times 10^{-7}$	Total ozone content in cm. at N.T.P.					
		Delhi				Poona	
		0·155	0·175	0·200	0·217	0·164	0·174
50°	0·625	2·773	2·738	2·703	2·652	2·774	2·738
60°·75	1·36	2·678	2·627	2·581	2·523	2·660	2·632
70°	2·40	2·528	2·456	2·397	2·324	2·495	2·457
80°	4·10	2·173	2·068	1·978	1·907	2·116	2·060
84°	4·98	1·933	1·840	1·770	1·704	1·845	1·790
86°·5	5·60	1·821	1·782	1·742	1·713	1·740	1·703
90°	6·56	1·928	1·910	1·893	1·873	1·812	1·785

Calculations were made assuming different ozone amounts in the different sections and adjusting them by trial and error till satisfactory agreement was reached between the observed and calculated values. Since the observed values also include a constant C which depends on instrumental factors, this constant has to be eliminated by making the observed and calculated values equal at some angle. The observed values extended only upto $Z = 50°$ for the Delhi curves except in the case of the curve for 0·175 cm. for which they extended upto 43°. For the Poona curves, observations are available even upto 20°. $Z = 50°$ would be a sufficiently good point to secure agreement between the observed and calculated values, since at such an angle, the value of log I/I′ depends very little on the height distribution of ozone but only on its total amount. Thinking that $Z = 0°$ might be an even better point to choose, the values of log I/I′ at $Z = 0°$ were determined by extrapolation from the observed curves. It was, however, found that when there was agreement at 0° and at values of Z equal to 80° and higher, it was not possible to obtain agreement at the intermediate points 50°, 60°, 70° whatever changes were made in the assumed distributions. The plot of the calculated values in the region 0°–50° also showed considerable differences from the observed or extrapolated curves.

From later systematic observations at Simla,[12] the trouble was traced to the effect of large particle scattering. Although the sky might be apparently clear and this effect negligible for *large* values of Z, it would assume considerable proportions as the sun approached the zenith. The result was that there was an increasingly greater proportion of longer wavelengths in the zenith-scattered light at small zenith distances of the sun than pure molecular scattering would give. This effect is more pronounced for the longer wavelengths 4450 and 3300 A (due to their greater separation and smaller ozone-absorption) than for the shorter wavelengths 3300 and 3110 A, but affects the shorter wavelengths also to some extent. As a result, at small zenith distances of the sun, there is a marked difference between the observed values of log I/I′ and the values calculated on the assumption of molecular scattering. This can be seen from Figs. 1 and 2.

Dobson took $Z = 37°·5$ as the point where the calculated and observed curves were made to coincide and whatever difference he found at this point between the slopes of the lines drawn through the observed and calculated points, he attributed to secondary scattering. Secondary scattering has undoubtedly some effect and would make the observed curve slightly less steep than the calculated one. But since secondary scattering affects both the wavelengths more or less to the same extent, the effect on the ratio log I/I′ may be expected to be small. An inspection of Figs. 1 and 2 giving the

curves for Delhi and Poona suggests that the discrepancies observed at these places are more pronounced than can be attributed to neglect of secondary scattering alone. Large particle scattering due to the presence of dust and haze in the atmosphere appears to be mainly responsible for the difference between the observed and calculated curves for small zenith angles of the sun.

It was decided to adopt Z= 50°, for which observations are available in all seasons, as the point where the observed and calculated curves should be made to coincide, and adjust the distribution of ozone so as to secure agreement at higher values of Z. Since the effect of large particle scattering becomes less important for values of Z higher than about 40°–45°, this procedure was considered satisfactory. The calculated and observed points are shown in Figs. 1 and 2 and it will be noted that the agreement is satisfactory in the region 50°–90°. This region alone is important for determining the height distribution of ozone.

Table V gives the amounts of ozone in cm. per km. height in the different sections obtained from the final calculated distributions corresponding to the different total ozone amounts. Since we have assumed uniform distribution of ozone within each layer, the centre of gravity of each layer is at its midpoint and the centre of gravity of the total atmospheric ozone can also be found easily by taking moments about the earth's surface. These are given at the bottom of Table V.

TABLE V

Amounts of ozone in cm. per km. height in different layers of the atmosphere over Delhi and Poona

Layer No.	Boundaries of layer in km.	Total ozone content in cm.					
		Delhi				Poona	
		0·155	0·175	0·200	0·217	0·164	0·174
6	45—54	0·0004	0·0004	0·0005	0·0005	0·0004	0·0004
5	36—45	0·0010	0·0010	0·0010	0·0012	0·0023	0·0024
4	27—36	0·0077	0·0080	0·0080	0·0080	0·0070	0·0075
3	18—27	0·0055	0·0070	0·0091	0·0104	0·0070	0·0075
2	9—18	0·0016	0·0020	0·0026	0·0030	0·0014	0·0014
1	0— 9	0·0010	0·0010	0·0010	0·0010	0·0001	0·0001
Average height of C. G. of ozone above sea-level in km.		26·3	25·9	25·3	25·1	28·1	28·0

Fig. 3 gives block diagrams of the vertical distributions of ozone at Delhi and Poona. Assuming uniform distribution within each layer, smooth curves of distribution can be drawn, care being taken to see that the areas under the smooth curve and the block diagram for each section are equal. Fig. 4 shows the smooth distribution curves so obtained for Delhi and Poona. The same figure also gives for comparison the distribution curves obtained at Arosa and Tromsø. The ratio of ozone to air by volume at different levels in the atmosphere was also calculated and the results are summarised in Table VI which gives the height distributions both of ozone amount per km. and of the ratio of ozone to air for fixed levels.

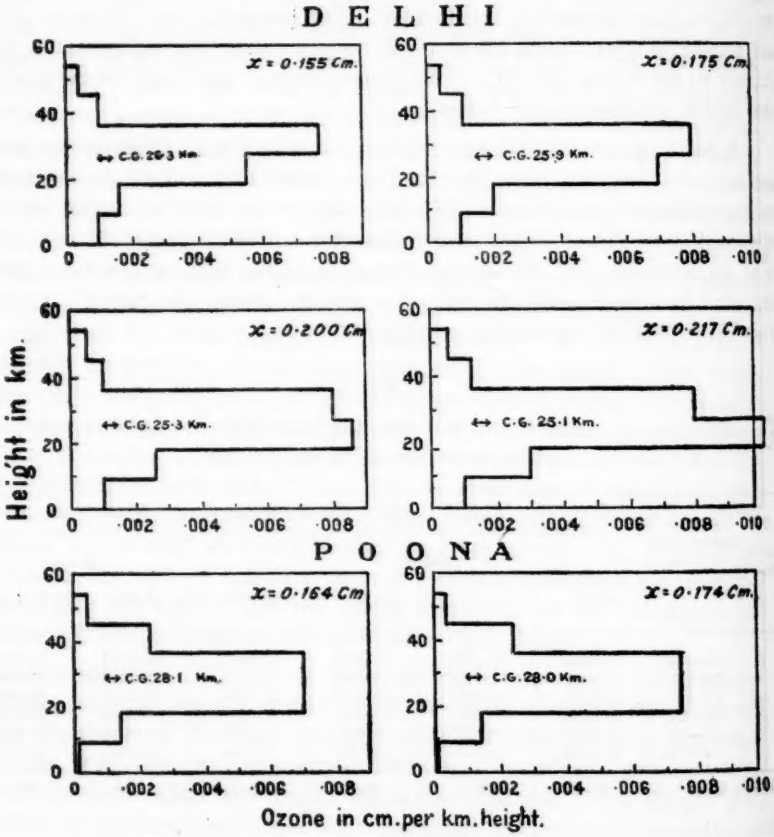

FIG. 3. Calculated vertical distributions of ozone over Delhi and Poona corresponding to different total ozone amounts x

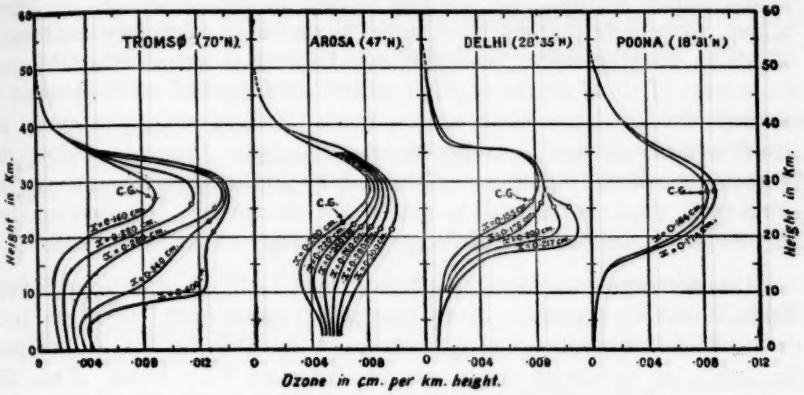

FIG. 4. Height distributions of atmoshperic ozone in different latitudes

TABLE VI

Height distribution of ozone over Delhi and Poona as cm. of ozone per km. height and as ratio R of ozone to air by volume

Height above M.S.L.	Delhi								Poona			
	0·155 cm.		0·175 cm.		0·200 cm.		0·217 cm.		0·164 cm.		0·174 cm.	
	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$
50	0·30	3·3	0·33	4·2	0·36	4·6	0·38	4·8	0·30	3·8	0·30	3·8
45	0·52	3·3	0·55	3·5	0·58	3·7	0·60	3·8	1·00	6·4	1·00	6·4
40	0·93	3·0	0·99	3·1	1·05	3·3	1·10	3·5	2·35	7·5	2·40	7·6
35	6·6	9·3	6·6	9·3	6·6	9·3	6·6	9·3	5·15	7·3	5·55	7·9
30	8·15	5·36	8·4	5·52	8·4	5·52	8·4	5·52	7·95	5·23	8·60	5·65
25	7·1	2·03	8·05	2·30	9·25	2·65	10·25	2·93	8·00	2·29	8·55	2·45
20	3·85	0·48	5·9	0·74	9·1	1·14	10·7	1·34	6·05	0·76	6·50	0·81
15	1·65	0·09	2·15	0·11	2·95	0·16	3·55	0·19	1·45	0·08	1·50	0·08
10	1·15	0·03	1·35	0·04	1·55	0·04	1·70	0·05	0·45	0·01	0·45	0·01
5	0·98	0·02	0·98	0·02	0·98	0·02	0·98	0·02	0·10	0·002	0·10	0·002
0	0·90	0·01	0·90	0·01	0·90	0·01	0·90	0·01	0·10	0·001	0·10	0·001

§7. DISCUSSION OF RESULTS

In a recent paper[8] on the day-to-day variations of ozone amount over Delhi, it was pointed out (i) that during the monsoon months, there was very little day-to-day variation of ozone in spite of the varying character

of the surface weather, and (ii) that during the season of western disturbances, there were marked fluctuations in ozone amount, deep cold waves of dry air being generally associated with increase in its quantity. In general, advent of air of northerly origin in the upper part of the troposphere is accompanied by increase in ozone amount and advent of southerly air (south-westerly or south-easterly or easterly) by a decrease. During the monsoon when the upper air movement is persistently from the east or south-east, there is very little day-to-day fluctuation. In Europe also, July-August is the season of minimum day-to-day variation of ozone.

Considering the vertical distribution over Delhi, it will be seen from Table V that the maximum ozone content lies either in the 18–27 km. layer or the 27–36 km. layer. The smooth curves for Delhi in Fig. 4 show that the height of maximum ozone content increases from about 22 km. for 0·217 cm. to 30 km. for 0·155 cm. The smooth curves for Poona show the corresponding height of maximum ozone content to be about 28–30 km. for 0·170 cm. of ozone.

In general, during winter and early hot season, any increase in ozone occurs mainly in the layer 18–27 km. and to a smaller extent in 9–18 km. It is interesting to compare these results with those obtained in higher latitudes at Arosa (47° N.) and Tromsø (70° N.). For the latter place, there are two sets of curves, one determined from the earlier short-term observations of Meetham and Dobson[6] using method B and the other from the later long-term observations of Tønsberg and Langlo[7] using method A. The later Tromsø curves show better agreement with the Arosa and Delhi curves and will be used for discussion here. Both at Arosa and Tromsø, a very important feature is that, while a layer of comparatively high ozone content lies between 25 and 30 km. for different total ozone amounts, the increases of ozone content for the higher ozone amounts occur mainly between 10 and 25 km. and to a less extent between 5 and 10 km.

Götz[11, 13] has made the suggestion that, at least for larger amounts of ozone, there are probably two maxima in the ozone distribution curves, one of which is between 25 and 30 km. and the other at a lower level. Recently, Durand and co-workers[14] have given a preliminary estimate of the vertical distribution of ozone in the atmosphere from measurements of the solar ultraviolet spectra obtained upto an altitude of 88 km. during a V-2 rocket flight over White Sands, New Mexico, when the total amount of ozone was 0·27 cm. Their curve shows two peaks in ozone concentration at about 17 and 25 km. The distribution curves obtained at Tromsø and Delhi also show the possibility of a similar feature of two maxima in the

case of higher ozone amounts, one at about 30 km. at both the places and the second between 10 and 15 km. at Tromsø and between 20 and 25 km. at Delhi. This point, however, requires further finer analysis and will no doubt be cleared up in due course.

As it stands, it appears to be a world-wide feature that there is a primary maximum of ozone content at 25–30 km. and that variations in ozone amount occur mainly between 10 and 25 km. and to a smaller extent between 5 and 10 km.

§8. Concluding Remarks

It will be useful to conclude with a very brief survey of the existing knowledge regarding the distribution of ozone in the earth's atmosphere. The following are the major features of the horizontal distribution:

(*a*) On the mean of the year, the ozone amount is least over equatorial regions, the average amount being about 0·18 cm. There is little variation over the tropics, but betwen 20° and 60°, it increases with latitude, the annual average being about 0·25 cm. at 60° and 70° N. Very low values of ozone seem to be common within the Arctic Circle during polar nights and the annual average may be expected to decrease on the poleward side of latitude 70°.

(*b*) In the northern hemisphere, the ozone amount is a maximum in March-April with a value of about 0·33 cm. at 70° N. In latitudes up to 60° N., the minimum occurs in October-November, but at Tromsø (70° N.), the month of minimum is delayed till December. In the region of Indian and Chinese monsoons, there is a tendency for the occurrence of a secondary minimum in July-August.

(*c*) The day-to-day variations are smallest throughout the northern hemisphere in July-August. They are in general a maximum in December-March when the horizontal gradients of ozone amount are a maximum. Near the Arctic Circle, violent fluctuations occur in December-January, changes of 0·10 to 0·15 cm. in one day being not uncommon.

Our knowledge regarding the vertical distribution has already been summarised. In the tropics, most of ozone is in the stratosphere and its amount is largely controlled by the photo-chemical actions causing its formation and decomposition.[15] These do not vary much during the year.* The tropospheric convective processes which carry water vapour and other

* Observations at Delhi and Poona show, however, that there is a regular daily variation in the amount of ozone in the tropics with a minimum at about midday. The average daily amplitude is 0·003 to 0·005 cm. of ozone.

particles into the upper part of the troposphere apparently tend to destroy any ozone that might come down from the stratosphere. Laboratory experiments support this. For example, A. W. Ewell[16] found that photochemical formation of ozone is decreased and photochemical decomposition increased, each by a factor 3, when dry air at room temperature was replaced by moist air.

The total amount of ozone over any place at a definite time is the sum of (i) the daily equilibrium amount produced by the photochemical action of sunlight and the recombination of ozone by collision processes with atomic oxygen and air molecules, and (ii) the accumulated ozone below the region of photochemical ozone formation which is largely screened from the decomposing radiation from the sun and which, owing to low temperature, undergoes only very slow thermal decomposition. The vertical distribution curve cannot be expected to be identical with that worked out on the basis of purely photo-chemical processes; there will always be more ozone content on the lower side of maximum owing to accumulation. The lower the tropopause and the greater the thermal stability of the troposphere, the larger will be the accumulation of ozone below the level of ozone formation. As is well known, Meetham[17] found a positive correlation of $+0{\cdot}8$ between ozone amount over Oxford and potential temperature at 18 km., and Dobson and Meetham[18] found a negative correlation of $-0{\cdot}7$ between ozone amount and height of tropopause. Meteorological factors mainly affect (ii) and it is mainly changes in accumulated ozone that show themselves when western depressions and cyclones cause changes in air-mass over a place.

Where, as in the tropics, or also in temperate latitudes in July and August, lapse-rates are high in the upper half of the troposphere and water vapour has the greatest chance of being systematically carried upward, the amount of accumulated ozone in the troposphere and the day-to-day changes in ozone amount remain persistently small. The most violent fluctuations occur where, as in the polar regions in December and January, there is a high gradient of photochemically formed ozone and also frequent changes of air-mass and accumulated ozone due to movement of depressions and storms.

The study of the vertical distribution of ozone in equatorial regions and of the daily variation of ozone on meteorologically undisturbed days in all parts of the world may be expected to throw further light on the causes of formation, accumulation and transport of ozone in the earth's atmosphere.

§9. Acknowledgment

The observations recorded in the present paper were made with the Dobson spectrophotometer belonging to the India Meteorological Department. The thanks of the authors are due to the Director-General of Observatories for the use of the instrument and for giving all necessary facilities. Thanks are also due to the Board of Scientific and Industrial Research for the award of a Research Fellowship to one of the authors during the period in which the work was done.

Summary

Observations of the light scattered from the clear blue zenith sky were made with Dobson's photo-electric spectrophotometer at Delhi (28° 35′ N.) and Poona (18° 31′ N.) during the periods November 1945 to March 1947 and February-March 1948, and these have been used to determine the height distributions of atmospheric ozone at these places. After using Dobson's method A in an exploratory way, the more detailed method B was used to calculate the vertical distributions from the observed Umkehr curves. Agreement between the observed and calculated points was obtained by trial and error at various zenith angles of the sun in the range 50°–90° where the effect of large particle scattering is negligible.

Distributions of ozone are given for total ozone amounts varying from 0·155 cm. to 0·217 cm. at Delhi, the average heights of ozone for these being from 26·3 km. to 25·1 km. A decrease in the total ozone amount is found to cause a rise in the centre of gravity. At Poona, distributions for ozone amounts 0·164 cm. and 0·174 cm. give a more or less fixed height of 28·0 km. for the centre of gravity.

The paper concludes with a brief survey of the distribution of ozone in the earth's atmosphere both in the horizontal and the vertical and shows that it is easier to understand the regional, seasonal and day-to-day variations of ozone if we separately consider the contributions to total ozone content over any place from the photo-chemical action of sunlight and from transport in the horizontal and vertical directions of the accumulated ozone below the level of primary ozone formation.

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ACETYLATION OF PHENOLS USING ACETIC ACID

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The use of acetic acid in the acetylation of the lower alcohols is well known. The acid has also been used for the acetylation of aliphatic hydroxy acids.[1] Its ability to introduce the acetyl group into the aromatic nucleus to produce acetophenones has been recently shown by Kosolapoff.[2] However, its use for the acetylation of phenols does not seem to have been investigated,[3] though a reference was made by Dusart and Bardy to the formation of phenyl acetate by the action of fuming hydrochloric acid at 180° on a mixture of acetic acid and phenol.[4] Under the conditions adopted by these authors, it is doubtful whether acetic acid actually exists as such, since, in the presence of dehydrating agents, it is known to be converted into acetic anhydride[5] or acetyl chloride, if hydrogen chloride is also present.[6]

The scope of the employment of glacial acetic acid for the acetylation of phenols has now been studied. The condensation has been carried out in the presence of phosphorus pentoxide under different conditions and the following results are obtained (table). Under the conditions of our experiments there is no indication of the formation of any acetic anhydride, and the acetylation seems to have been effected by the direct elimination of a molecule of water between the phenol and acetic acid.

No.	Phenol	Glacial acetic acid	Phosphorus pentoxide	Temperature	Duration of reaction in hours	Yield of the acetyl derivative in g.
1	9·4 g.(0·1 mole)	6·0 g. (0·1 mole)	7 g (0·05 mole)	0° C.	24	3·0
2	,,	,,	,,	35°	24	5·0
3	,,	,,	,,	100°	1	5·5
4	,,	,,	,,	100°	2	5·5
5	,,	,,	,,	100°	3	5·5
6	,,	,,	14 g. (0·1 mole)	100°	1	5·0
7	,,	,,	,,	100°	2	5·0
8	,,	12·0 g. (0·2 mole)	7 g. (0·05 mole)	100°	1	4·5
9	,,	18·0 g. (0·3 mole)	,,	100°	1	4·5

From the above results, the condensation seems to take place best when (1) the reactants are present in equimolecular proportions, (2) the condensing

agent is in half molecular amounts and (3) the heating is for one hour at 100° C. Since the mixture of the reactants with phosphorus pentoxide at the room temperature produces considerable local heating and consequent decomposition, the procedure followed has been to add a cooled mixture of the reactants to well-cooled phosphorus pentoxide, further cooling the mixture in ice-water during addition. Adopting this procedure the acetylation of various simple phenols has been carried out and the acetyl derivatives are produced in 10 to 40 per cent. yields.

Though only an equimolecular amount of acetic acid takes part in the condensation, its presence in excess does not seriously affect the yields. In the case of solid phenols, consequently, acetic acid has been taken in excess to keep the phenol in solution.

Zinc chloride also effects the condensation, though the yields are lower than when phosphorus pentoxide is used.

Experimental

Phenyl acetate.—Dry phenol (9·4 g., 0·1 mole) and glacial acetic acid (6·0 g., 0·1 mole) were mixed in a dry conical flask and cooled to zero degrees in ice. Similarly phosphorus pentoxide (7 g., about 0·05 mole) was cooled in a dry acetylation flask provided with an air-condenser and anhydrous calcium chloride tube, and the mixture of phenol and acetic acid was then carefully added to it. During the addition the mixture was shaken vigorously and cooled to avoid local development of heat and consequent decomposition. It was then kept on a water-bath the temperature of which was slowly raised to the boiling point during the course of half an hour. Heating was continued for an hour longer. The mixture was then cooled and treated with crushed ice (200 g.). When it attained the laboratory temperature, it was extracted twice with ether. From the combined ether extract (200 c.c.), the unreacted phenol was removed by extraction with 10 per cent. sodium hydroxide (50 c.c.). The ether solution was then washed with water and dried over anhydrous sodium sulphate. On the removal of the solvent, phenyl acetate was obtained, and purified by redistillation. B.P. 196° C. The yield was 5·5 g.

Using anhydrous zinc chloride as the condensing agent in place of phosphorus pentoxide, the yield of phenyl acetate was 3·0 g. from 9·4 g. of phenol.

m-Tolyl acetate.—The same procedure as in the case of phenyl acetate was followed. From 10 g. of *m*-cresol, 6 g. of glacial acetic acid and 7 g. of phosphorus pentoxide, heating for an hour on the boiling water-bath, 4·7 g. of the ester boiling at 212° C. was obtained.

Resorcinol diacetate.—By adopting the general procedure described above, the acetylation of resorcinol was tried. From 11 g. of resorcinol and 12 g. of glacial acetic acid, only 1·5 g. of diacetyl resorcinol, boiling at 278° C., was obtained.

Since there was the chance for mono-acetylation also to take place, the alkaline extract from the ethereal solution containing the reaction products was diluted with water to 200 c.c., acidified with hydrochloric acid and then extracted with ether, when a small amount of resorcinol monoacetate, (0·5g.), b.p. 183° C., was obtained [Found: C, 63·35; H, 5·41; $C_6H_4(OH)(OCOCH_3)$ requires C, 63·15 and H, 5·26%]. The oil was somewhat soluble in water and freely in alkalis and the aqueous solution gave a purplish violet colour with ferric chloride.

Catechol diacetate.—When the mixture of catechol (11 g.) and acetic acid (12 g.) was added to phosphorus pentoxide (7 g.) as before and heated for an hour on a boiling water-bath, 1 g. of the diacetyl derivative, melting at 63° C., was obtained. Mixed m.p. with the sample obtained from catechol through the action of acetic anhydride and anhydrous sodium acetate was undepressed. No lower product of acetylation could be isolated.

Pyrogallol triacetate.—The reaction between pyrogallol and glacial acetic acid was carried out as in the previous case. Only 1 g. of the triacetyl derivative, m.p. 165° C., was obtained from 12·6 g. of pyrogallol and 18 g. of glacial acetic acid.

α-Naphthyl acetate.—From 14·5 g. of α-naphthol and 12 g. of glacial acetic acid, 3 g. of the acetate was obtained. It melted at 48–49° C.

β-Naphthyl acetate.—4·0 g. of the acetate, m.p. 70° C., was obtained from 14·5 g. of β-naphthol and 12 g. of glacial acetic acid.

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SUMMARY

Acetylation of phenols with glacial acetic acid in presence of phosphorus pentoxide gives the *O*-acetyl derivatives in yields of 10 to 40 per cent.

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ELASTIC CONSTANTS OF ALUMINA

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1. Introduction

Corundum or alumina, Al_2O_3, is well known as a naturally occurring precious stone from ancient times. Its crystal structure belongs to the space group $D_3^6{}_d$ of the trigonal system. It is remarkable for its hardness being next only to diamond. Many of its physical properties have been studied extensively. Amongst various others, R. S. Krishnan (1947) has studied its Raman effect with thoroughness. Deutschbein (1932, 33, 34), Venkateswaran (1935) and Anna Mani (1942) investigated the luminescence properties of alumina containing chromic oxide as an impurity. But the exact elastic behaviour of alumina in terms of the characteristic constants of that group has not yet been studied. In fact in the literature, data for its Young's modulus along the optic axis (Auerbach) and compressibility (Bridgmann, 1933) only are available. Because of its many interesting properties, it was considered desirable to determine all the elastic constants of the crystal. This has been carried out and the results are presented in this paper.

2. Procedure of the Experiment

Naturally occurring corundum being unavailable, synthetic alumina is used in the present investigation. The latter is available in the form of boules grown out of molten aluminium oxide by a special process. Though it does not crystallize in the process with all its faces marked out, its crystalline character is completely established. As it is, a specimen in the form of approximately a semi-cylindrical boule is used in the experiment. To cut the necessary sections, a knowledge of all the crystal axes is necessary. But in the specimen, only the optic axis is known by a preliminary experiment with a pair of polaroids, the details of which are given in a latter section. The procedure of the investigation under such circumstances is briefly outlined below:

The complete matrix of the elastic constants of the crystal is given by

$$\begin{vmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & 0 & c_{14} & c_{66} \end{vmatrix}$$

in which $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ and which has thus six independent elastic constants.

Referring the crystal to the orthohexagonal axes such that the x-y-plane is a plane of symmetry according to the notation of Voigt, the longitudinal and the torsional wave velocities in any direction may be obtained either from the classical Christoffel's equations or by transforming the appropriate fourth order tensor component in the above matrix. Considering the extreme simplicity, the latter method is adopted in what follows.

We suppose the axes to be transformed so that the new X_3 axis, *i.e.*, X_3' with reference to the old orthogonal axes X_1, X_2, X_3 coincides with the arbitrary direction under consideration. The dashed system of co-ordinates represent the new disposition of the axes with respect to the old undashed ones. The two systems are related by the usual cosine scheme given below, defining the new X'_3 direction by the direction cosines a_{13}, a_{23} and a_{33}.

	X_1'	X_2'	X_3'
X_1	a_{11}	a_{12}	a_{13}
X_2	a_{21}	a_{22}	a_{23}
X_3	a_{31}	a_{32}	a_{33}

Now the appropriate constant for the longitudinal wave travelling along X_3' is C_{33}', and that for a plate twisted about X_3' is C_{44}'. After transforming the particular components to the new axes and remembering which of the c_{ij}'s are zero in the matrix, we get:

$$c'_{33} = c_{11}(1 - a_{33}^2)^2 + c_{33}a_{33}^4 + (4c_{44} + 2c_{13})\,a_{33}^2(1 - a_{33}^2) + 4c_{14}a_{23}a_{33}(3a_{13}^2 - a_{23}^2) \qquad \text{(i)}$$

$$\begin{aligned} c_{44}' = {} & c_{11}(a_{12}^2a_{13}^2 + a_{22}^2a_{23}^2) + 2c_{12}a_{12}a_{13}a_{22}a_{23} + \\ & 2c_{13}[a_{32}a_{33}(a_{12}a_{13} + a_{22}a_{23})] + \\ & c_{14}[4a_{12}a_{13}(a_{22}a_{33} + a_{23}a_{32}) + 2(a_{12}^2a_{23}a_{33} + \\ & \quad a_{12}^2a_{22}a_{32} - a_{22}^2a_{23}a_{33} - a_{22}a_{23}^2a_{32})] + \\ & c_{33}(a_{32}^2a_{33}^2) + c_{44}[(a_{22}a_{33} + a_{23}a_{32})^2 + (a_{12}a_{33} + a_{13}a_{32})^2] + \\ & c_{66}(a_{12}a_{23} + a_{13}a_{22})^2. \end{aligned} \qquad \text{(ii)}$$

From equation (i) we have for a Z-cut plate, $a_{33} = 1$, $a_{23} = a_{13} = 0$ so that the longitudinal constant is c_{33}. Also c_{44} can be shown to be a doubly degenerate constant for the torsional mode for the same plate. For any plate

containing the Z- or X_3 axis, *i.e.*, its normal is perpendicular to Z or X_3 axis, we have $a_{33} = 0$ and the longitudinal constant is therefore c_{11} irrespective of the inclination of the plate to the X_1 and X_2 axes. We will now show that similarly the shear constants of such a plate are the same provided the plate contains the X_3 axis in its plane, whatever be the inclination of the plate to the other axes.

Considering a plate twisted about the X_3' axis, which lies in the X_1X_2 plane and makes an angle ϕ with X_1 we see that the X_3' axis can be brought into that position in two ways, illustrated by the two Figures 1 (*a*) and 1 (*b*). In Fig. 1 (*a*) the X_3 axis is first rotated through $\frac{\pi}{2}$ in the X_1X_3 plane and then through ϕ in the X_1X_2 plane. Similarly the other Fig. 1 (*b*) can be explained. The direction cosines for the two positions are given respectively by the two schemes 2 (*a*) and 2 (*b*) below.

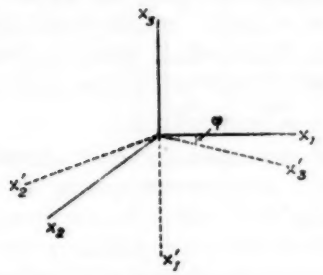

Fig. 1(a)

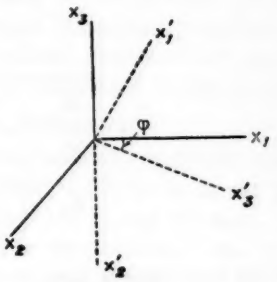

Fig. 1(b)

	X_1'	X_2'	X_3'
X_1	O	−S	C
X_2	O	C	S
X_3	−1	O	O

	X_1'	X_2'	X_3'
X_1	S	O	C
X_2	−C	O	S
X_3	O	−1	O

S and C are abbreviations for $\sin\phi$ and $\cos\phi$ respectively.

Using 2 (*a*) in equation (ii) we get after reduction

$$c_{44}' = 2\sin^2\phi\cos^2\phi \cdot c_{11} - 2c_{12}\sin^2\phi\cos^2\phi + c_{66}(\sin^2\phi - \cos^2\phi)^2 \qquad \text{(iii)}$$

Since $\sin 2\phi = 2\sin\phi\cos\phi$; $\cos 2\phi = \cos^2\phi - \sin^2\phi$, and $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ we get (iii) as

$$c_{44}' = \tfrac{1}{2}(c_{11} - c_{12}) = c_{66} \qquad \text{(iv)}$$

Using 2 (*b*) in (ii) we get

$$c_{44}' = c_{44}(\cos^2\phi + \sin^2\phi) = c_{44}. \qquad \text{(v)}$$

Thus a plate perpendicular to the X_3 axis, the so-called Z-cut, and another containing the Z-axis in its plane would together yield four constants, *viz.*, c_{11}, c_{12}, c_{33} and c_{44} without necessitating a knowledge of the X_1 and X_2 axes of the crystal.

But the size, shape and the peculiar disposition of the optic axis in the crystal boule made it less easy to cut an exact Z-cut plate. Hence a section as nearly normal to the X_3 axis as possible is cut. To get the various constants, we have to cut a number of sections with different and convenient angles to the optic axis. The theory of the procedure is given below, pending the experimental technique to a latter section.

If the normal to a plate be defined by the polar co-ordinates r, θ, ϕ, we have for its direction cosines:

$$a_{13} = \sin\theta\cos\phi; \quad a_{23} = \sin\theta\sin\phi; \quad a_{33} = \cos\theta.$$

If the plate is cut with its plane making an angle $(90 - \theta)$ with the optic axis, its normal will have a known angle θ and an unknown angle ϕ for its angular polar co-ordinates. Six sections inclined at various angles are cut and ground to uniform thickness. The sections and the direction cosines of their normals are given below in Table I in which $\theta_1 = 0$; $\theta_2 = 14° 30'$;

TABLE I

No.	Polar co-ordinates of X_3'	a_{13}	a_{23}	a_{33}
1	(θ_1, ϕ)	0	0	1
2	(θ_2, ϕ)	$\sin\theta_2\cos\phi$	$\sin\theta_2\sin\phi$	$\cos\theta_2$
3	(θ_3, ϕ)	$\sin\theta_3\cos\phi$	$\sin\theta_3\sin\phi$	$\cos\theta_3$
4	(θ_4, ϕ)	$\sin\theta_4\cos\phi$	$\sin\theta_4\sin\phi$	$\cos\theta_4$
5	(θ_5, ψ)	$\sin\theta_5\cos\psi$	$\sin\theta_5\sin\psi$	$\cos\theta_5$
6	$(\theta_5, 90+\psi)$	$-\sin\theta_5\sin\psi$	$\sin\theta_5\cos\psi$	$\cos\theta_5$

$\theta_3 = 29°$; $\theta_4 = 151°$; $\theta_5 = 45°$; the method of determining which being given in the experimental technique. In cutting the last two sections, the same angle ϕ could not be maintained as the specimen became very small. Hence another symbol ψ is written for the co-ordinate ϕ. $a_{13} = a_{23} = 0$ for the first plate because $\theta_1 = 0$.

Hence from the first plate we get the constants c_{11}, c_{44} and c_{66} and hence c_{12}. From the plates 2, 3 and 4, we get using the relation (i), the following equations:

$$_2c_{33}' = c_{11}\sin^4\theta_2 + c_{33}\cos^4\theta_2 + (4c_{44} + 2c_{13})\sin^2\theta_2\cos^2\theta_2 + 4c_{14}\sin^3\theta_2\cos\theta_2\sin\phi\,(3\cos^2\phi - \sin^2\phi) \quad \text{(vi)}$$

$$_3c_{33}' = c_{11}\sin^4\theta_3 + c_{33}\cos^4\theta_3 + (4c_{44} + 2c_{13})\sin^2\theta_3\cos^2\theta_3 + 4c_{14}\sin^3\theta_3\cos\theta_3\sin\phi\,(3\cos^2\phi - \sin^2\phi) \quad \text{(vii)}$$

$$_4c_{33}' = c_{11}\sin^4\theta_4 + c_{33}\cos^4\theta_4 + (4c_{44} + 2c_{13})\sin^2\theta_4\cos^2\theta_4 + 4c_{14}\sin^3\theta_4\cos\theta_4\sin\phi\,(3\cos^2\phi - \sin^2\phi) \quad \text{(viii)}'$$

where $\theta_2 = 14° 30'$; $\theta_3 = 29°$; $\theta_4 = 151°$. Now since $\theta_4 = 151°$, we get (viii)′ merely as

$$_4c'_{33} = c_{11}\sin^4\theta_3 + c_{33}\cos^4\theta_3 + (4c_{44} + 2c_{13})\sin^2\theta_3\cos^2\theta_3 - 4c_{14}\sin^3\theta_3\cos\theta_3\sin\phi\,(3\cos^2\phi - \sin^2\phi) \quad \text{(viii)}$$

The extra suffixes of c'_{33} indicate plate number. Since the left-hand side is experimentally determined, we can solve (vi), (vii) and (viii) for c_{33} and c_{13} by eliminating $c_{14}\sin\phi\,(3\cos^2\phi - \sin^2\phi)$ from the equations by the usual methods, and using the values of c_{11}, c_{44} and c_{12} determined from the first plate.

To determine c_{14} we have from the plates 5 and 6,

$$_5c'_{33} = \tfrac{1}{4}(c_{11} + c_{33} + 4c_{44} + 2c_{13}) + c_{14}\sin\psi\,(3\cos^2\psi - \sin^2\psi) \quad \text{(ix)}$$

$$_6c'_{33} = \tfrac{1}{4}(c_{11} + c_{33} + 4c_{44} + 2c_{13}) + c_{14}\cos\psi\,(3\sin^2\psi - \cos^2\psi) \quad \text{(x)}$$

whence we get after trigonometrical reduction:

$$a = c_{14}\sin 3\psi, \quad \text{(xi)}$$

$$b = -c_{14}\cos 3\psi \quad \text{(xii)}$$

where

$$a = {}_5c_{33}' - \tfrac{1}{4}(c_{11} + c_{33} + 4c_{44} + 2c_{13})$$

$$b = {}_6c_{33}' - \tfrac{1}{4}(c_{11} + c_{33} + 4c_{44} + 2c_{13})$$

Hence

$$a/b = -\tan 3\psi. \quad \text{(xiii)}$$

Since a and b are known, 3ψ can be calculated and hence c_{14} is determined from (xi) or (xii). Thus all the constants are determined from the six plates.

3. Experimental Technique

The determination of the optic axis and the measurement of the various angles in Table I are effected by means of a pair of ordinary polaroids, using the property that if the polaroids are initially set for crossing with light polarised in a vertical or horizontal plane, and the specimen immersed in benzene for obvious optical reasons is then introduced between them, the crossing remains perfect for any amount of rotation of the specimen about a horizontal axis along the path of the ray only if the axis is the direction of the optic axis also. Proceeding in the above manner, the optic axis was found to lie in the plane surface of the semi-cylinder, inclined at an angle

to the lengthwise axis of the boule. Since no other axis of the crystal can be determined by any optical method, the preparation of the sections necessary becomes a little more complicated than if the axes are known as usual in a natural crystal. The details of the sections cut are given elsewhere. It is enough to point out that the sections are cut with their normals inclined at definite known angles to the optic axis by carefully fixing the specimen by gadgets on a cutting machine. After cutting and grinding the sections, the inclination of the normal to the plate thus prepared to the optic axis is again determined by means of the polaroids, using the same principle as above. The plate is fixed in a special crystal holder attached to a goniometer and immersed in benzene for the purpose. The optic axis is first brought into a horizontal plane by fixing the plate vertical with its plane parallel to the plane of the polaroids, and is then rotated in its own plane until the optic axis is in a horizontal plane. The plate is then rotated about a vertical axis until light passes along the optic axis. The angle of rotation after correcting for the difference in the refractive indices of the specimen and the surrounding medium gives the inclination of the normal to the optic axis. It is found that the angles thus measured agreed with those at which they were fixed within $\pm 1°$. Finally it is also established that there is no twinning in the crystal by taking Laue photographs for the thinnest plate. Incidentally the angle which the normal to it makes with the optic axis is also verified in the process and comes out as 14° 30′ while the optical method gives it as 14°.

A Z-cut tourmaline plate of uniform thickness as per the method described by the author in a previous publication (1948) is used as a source of ultrasonic waves, the plate being driven by a Hartley oscillator using R.C.A. 807 valve under rated conditions.

4. Experimental Results

Table II gives the experimental results obtained.

TABLE II

No.	Description of the plate	Thickness in mm.	Mode	Corresponding velocity of the wave in meters per second	Effective elastic constant in 10^{11} dynes/cm.^{2}
1	$(0, \phi)$	1·885	$(l)c_{11}$	10790	46·6
2	$(0, \phi)$	1·885	$(t)c_{44}$	7674	23·51
3	$(0, \phi)$	1·885	$(t)c_{66}$	2057	16·93
4	$(14° 30', \phi)$	1·17	$(l)_2c'_{33}$	11370	51·72
5	$(14° 30', \phi)$	1·17	(t)	7714	23·81*
6	$(29°, \phi)$	2·235	$(l)_3c_{33}'$	11240	50·47
7	$(151°, \phi)$	2·11	$(l)_4c_{33}'$	11840	56·07
8	$(45°, \phi)$	3·22	$(t)_5c_{33}'$	10880	47·41
9	$(45°, 90+\phi)$	2·32	$(l)_6c_{33}'$	10800	46·69

In the above table, *l* denotes longitudinal and *t*, torsional modes. Using the relations developed in the previous sections, the following values are finally obtained, all expressed in units of 10^{11} dynes/cm.^{2}

$$c_{11} = 46{\cdot}6 \qquad c_{14} = 9{\cdot}4$$
$$c_{12} = 12{\cdot}7 \qquad c_{33} = 50{\cdot}6$$
$$c_{13} = 11{\cdot}7 \qquad c_{44} = 23{\cdot}5$$
$$(\psi = -14°)$$

Using these values, the angle ϕ of plates (2), (3) and (4) in Table I come out as 14° 21′, 15° 54′, and 16° 22′, which differ at most by little more than 2° and hence ϕ is reasonably constant as assumed in the equation, the difference of 2° being due to experimental difficulties of cutting and grinding.

We can also see from the row marked with * in Table II that the torsional mode of the approximately Z-cut plate is very nearly the same as c_{44}, which is as it should be since the torsional mode of an actual Z-cut is c_{44}.

The principal Young's modulus along the Z-axis of a naturally occurring crystal of corundum has been determined by Auerbach and its value comes out as 53·1 in the above units.

The elastic moduli, *s*'s are also calculated using the relations (Voigt)

$$s_{11} + s_{12} = \frac{c_{33}}{c} \qquad s_{11} - s_{12} = \frac{c_{44}}{c'}$$

$$s_{13} = -\frac{c_{13}}{c} \qquad s_{14} = -\frac{c_{14}}{c'}$$

$$s_{33} = \frac{c_{11} + c_{12}}{c} \qquad s_{44} = \frac{c_{11} - c_{12}}{c'}$$

where
$$c = (c_{11} + c_{12})\, c_{33} - 2c_{13}^2$$
$$c' = (c_{11} - c_{12})\, c_{44} - 2c_{14}^2.$$

The values of the *s*'s in units of 10^{-13} cm.^{2} dyne^{-1} are

$$s_{11} = 2{\cdot}84 \qquad s_{14} = -1{\cdot}52$$
$$s_{12} = -0{\cdot}95 \qquad s_{33} = 2{\cdot}21$$
$$s_{13} = -0{\cdot}47 \qquad s_{44} = 5{\cdot}47.$$

Since the Young's modulus in any direction is $E' = \frac{1}{s_{33}'}$ we get its value as $45{\cdot}3 \times 10^{11}$ dynes cm.$^{-2}$ along the Z-axis. The lower value for the Young's modulus than the one determined by Auerbach is probably due to the fact that he used naturally occurring specimen while the author used a synthetic specimen grown out of molten alumina.

Using the relation for the compressibility

$$\beta = \frac{c_{11} + c_{12} + 2c_{33} - 4c_{13}}{c},$$

we get $\beta = 4{\cdot}11 \times 10^{-13}$ cm.^{2} dyne^{-1}. Madelung's and Fuch's value for the same is 3·8 in the above units. For comparison Madelung and Fuch's value for sapphire is also worked out into the same units and it is $4{\cdot}3 \times 10^{-13}$. Bridgman's value for synthetic sapphire for compressibility is 3·24.

As a whole it can be seen that the elastic constants are very high keeping in qualitative conformity with the fact that the substance is the hardest next to diamond.

5. Elasticity Surfaces

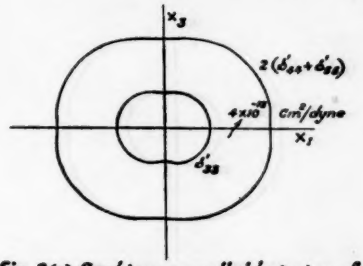

Fig. 2 (a) Sections parallel to (010) surface.

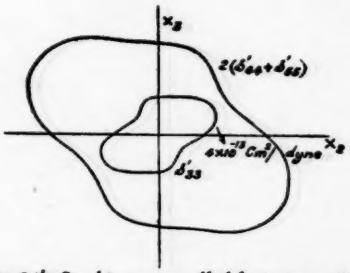

Fig. 2 (b) Sections parallel to (100) Surface.

Since previous measurements of elasticity of alumina are very few, the polar diagrams of the elasticity surfaces for the crystal for the two interesting sections in it are also drawn in Figs. 2 (*a*) and 2 (*b*). The relations (Wooster)

$$s_{33}' = s_{11}(1 - a_{33}^2)^2 + s_{33}a_{33}^4 + (4s_{44} + 2s_{13})\,a_{33}^2(1 - a_{33}^2) + 4s_{14}a_{23}a_{33}(3a_{13}^2 - a_{23}^2) \qquad \text{(xiv)}$$

$$2(s_{44}' + s_{55}') = 2[(s_{44} + s_{66} + (s_{44} - s_{66})\alpha_{33}^2 + (s_{11} + s_{33} - 4s_{44} - 2s_{13}) \times \alpha_{33}^2(1 - \alpha_{33}^2) - 4s_{14}\alpha_{23}\alpha_{33}(3\alpha_{13}^2 - \alpha_{23}^2)] \quad \text{(xv)}$$

being respectively for a long thin plate and for twisting of a cylinder parallel to X_3' have been used to draw the surfaces, bearing in mind the difference in the notations adopted by Voigt and Wooster. The radius vector to any point on the curve gives the magnitude of the appropriate modulus in that direction.

The author expresses his gratitude to Prof. R. S. Krishnan for his very kind guidance and encouragement.

6. Summary

The elastic constants of alumina have been determined by the ultrasonic method, the values being

$c_{11} = 46{\cdot}6$ $\quad$ $c_{14} = 9{\cdot}4$

$c_{12} = 12{\cdot}7$ $\quad$ $c_{33} = 50{\cdot}6$

$c_{13} = 11{\cdot}7$ $\quad$ $c_{44} = 23{\cdot}5$

in units of 10^{11} dynes cm.$^{-2}$ The elastic surfaces are drawn.

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SYNTHESIS OF COMPOUNDS RELATED TO ERYTHRINA ALKALOIDS—PART I

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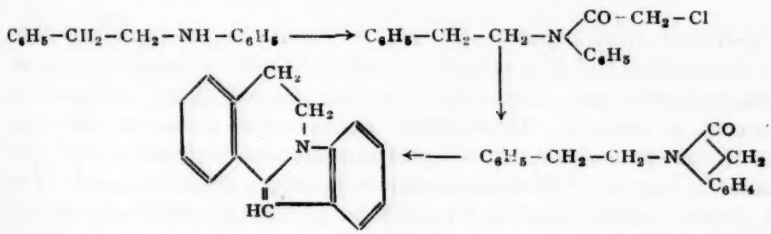
Altamirano[1] showed that extracts of the seeds of *Erythrina americana* Mill produce a strong curare action, *i.e.*, a selective paralysing action on motor nerve endings of striated muscle. After many years Ramirez and Rivero,[2] and Lehman[3] confirmed the curare action of the crude extracts. Folkers and his collaborators[4] carried out a very detailed examination of several species of Erythrina leading to the isolation and characterisation of a number of well-defined alkaloids. The oxidation of erythramine methohydoxide by aqueous permanganate gave hydrastic acid. The nitrogen atom was found to be tertiary and common to two nuclei. Alkaline fusion of some of the alkaloids yielded indole. On the basis of the above and examination of ultraviolet absorption spectra, a constitution incorporating a hydrindole nucleus and a hydro-isoquinoline nucleus, with the nitrogen atom common to the two heterocyclic rings was suggested.

The present work was undertaken with the object of synthesising condensed ring systems of the above type leading ultimately to the synthesis of the alkaloids. The method adopted is cyclodehydration of N-β-phenyl-ethyl indole by the application of Bischler Napieralsky reaction:



The synthesis of the substituted oxindole by the condensation of oxindole with β-phenyl ethyl chloride did not give satisfactory encouragement. The nitrogen substituted oxindole was obtained in fairly good yield by the ring closure of N-chlor acetyl-N-β-phenyl ethyl aniline, which in turn was obtained by chloracetylation of β-phenyl ethyl aniline. The oxindole ring closure proceeded with facility and the further ring closure was effected by phosphorus oxychloride in boiling benzene.

The synthesis of other members of this group is in progress.

Experimental

N-β-Phenyl ethyl aniline.—A mixture of 42·1 g. (0·3 mol.) of phenyl ethyl chloride and 83·7 g. (0·9 mol.) of aniline was boiled under reflux for two hours. The crystalline hydrochloride that separated out on cooling was dissolved in water and basified with sodium hydroxide. The liberated base was dried over anhydrous potassium carbonate and the fraction distilling at 185–190°/10 mm. was redistilled yielding a colourless viscous oil boiling at 186–187°/10 mm. (48 g., 80%).

Found: C, 85·02%; H, 7·62%. $C_{14}H_{15}N$ requires 85·27% and 7·61%.

N-Chloracetyl-N-β-phenyl ethyl aniline.—49·2 g. (0·25 mol.) of phenyl ethyl aniline were dissolved in 40 c.c. of pure acetone and 25 c.c. of dry pyridine added. This solution, kept cooled in an ice-bath, was treated drop-wise with a solution of 32 g. (excess) of chloracetyl chloride in acetone under stirring. The reaction mixture, which was almost a solid mass, was allowed to remain at room temperature (28°) for one hour and then heated for ten minutes on a boiling water-bath. The cooled product was treated with dilute acid and the product that separated out as an oil soon solidified to a mass of crystals. It crystallised from methyl alcohol in colourless crystals melting at 75–76° (60 g., 87%). The substance produces a very unpleasant sensation in contact with the skin.

Found: C, 70·20%; H, 6·09%. $C_{16}H_{16}NOCl$ requires 70·20% and 5·85%.

N-β-Phenyl ethyl oxindole.—27·4 g. (0·1 mol.) of N-chloracetyl-N-β-phenyl ethyl aniline and 26 g. (about 0·2 mol.) of freshly prepared anhydrous aluminium chloride were intimately mixed and heated, under exclusion of moisture, in an oil-bath. The vigorous reaction that ensued at 100° was allowed to subside and then the temperature was slowly raised to 140° and maintained at that point till the evolution of hydrogen chloride ceased. The cooled, brown viscous mass was poured on to ice, acidified with hydrochloric acid and allowed to stand till the oily product that separated solidified. On repeated crystallisation (animal charcoal) a colourless product was obtained melting at 95° (18 g., 75%).

Found: C, 80·93%; H, 6·45%. $C_{16}H_{15}NO$ requires 81·01% and 6·32%.

Molecular weight (cryoscopic method-benzene) 241. The substance dissolved in cold concentrated sulphuric acid forming a colourless solution which turns intensely red on treatment with powdered potassium dichromate.

Cyclisation of N-β-phenyl ethyl oxindole.—10 g. of the oxindole dissolved in 200 c.c. of dry benzene was treated with 15 g. of phosphorus oxychloride and refluxed on a boiling water-bath till the evolution of hydrogen chloride practically ceased (6 hours). The cooled solution was treated with crushed ice, the benzene layer washed free of acid, dried and the solvent removed. The residue, on standing, became semi-solid. It was stirred up with a little glacial acetic acid, collected and washed with a small volume of ethyl acetate, when a nearly white crystalline powder was obtained. The washings yielded about 2 g. of the unchanged oxindole. The product, crystallised from a mixture of benzene and absolute alcohol, separated in white plates melting at 200–201° (1·5 g.).

Found: C, 87·84%; H, 6·12%. $C_{16}H_{13}N$ requires 87·67% and 5·93%.

The substance dissolved in cold concentrated sulphuric acid forming a colourless solution, in the cold, with a strong bluish violet fluorescence. On warming, this becomes intensely green. The cold sulphuric acid solution becomes deep blue with dichromate.

Summary

The synthesis of a heterocyclic ring system containing an iso-quinoline ring fused to an indole ring, with the nitrogen atom common to the two rings, is reported.

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CONDENSATION OF ALDEHYDES WITH AMIDES

Part XVII. Of 5-Chloro- and 3: 5-Dichlorosalicylaldehyde

ADDENDUM

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To Part XVII already published,[19] four more condensations are to be added, *viz.*, two more condensations of each of the two aldehydes with phenylacetamide and cinnamamide. In all the four cases the products have been of the *-bis* form, and the yields have generally increased on conducting the condensations a little above the water-bath temperature: indeed quantitative yields were obtained in the 3: 5-dichlorosalicylaldehyde-cinnamamide condensation conducted at 100–110°. Cinnamamide, in fact, condensed more quickly than most of the other amides. The influence of the chlorine on the aldehyde was most marked in the case of the dichlorosalicylaldehyde, which often gave higher yields than were given by salicylaldehyde. The general conclusions drawn earlier[19] are thus confirmed.

Experimental

Condensation with Phenylacetamide

5-*Chlorosalicylaldehyde* (0·40 g.) and phenylacetamide (0·675 g.) (1 : 2 mol.) were heated together on water-bath (98°) for ten hours. A homogeneous liquid was soon formed but it changed into a solid after six hours' heating. It was a hard yellow mass difficult to break. After standing overnight, it was extracted with water, washed with ether and then with hot water, when a crude product melting at 190–195° was obtained. It was white and was crystallised from alcohol in needle crystals: m.p. 201°. It weighed 0·35 g. Cl, found: 9·010 per cent. Chlorosalicylidene-*mono*-phenylacetamide $C_{15}H_{12}O_2NCl$ requires 12·18%; Chlorosalicylidene-*bis*-phenylacetamide $C_{23}H_{21}O_3N_2Cl$ requires 8·69%. The product was thus the *bis*-compound, and the yield was 35·5% of theory.

When the experiment was repeated at 100–110°, the yield increased to 57·46%. It decolourised potassium permanganate (alkaline), gave no red colour with concentrated sulphuric acid and had the usual solubility.

3: 5-*Dichlorosalicylaldehyde* (0·5 g.) and phenylacetamide (0·675 g.), (1 : 2 mol.), were heated on water-bath for ten hours and, as before, gave

after six hours a hard yellow solid. After the same treatment as above a crude product was obtained melting at 180–190°; on recrystallisation from alcohol it came out in white needle crystals melting at 195°. It weighed 0·30 g.

Cl, found: 16·16%; dichlorosalicylidene-*mono*phenylacetamide $C_{15}H_{11}O_2NCl_2$ requires 23·05%; dichlorosalicylidene-*bis*phenylacetamide $C_{23}H_{20}O_3N_2Cl_2$ requires 16·03%. The product was thus the *bis*-compound and the yield was 25·86%.

Heating in the same way at 100–110° raised up the yield to 86·24%.

In the other properties it completely resembled the first compound above.

Condensation with cinnamamide

5-*Chlorosalicylaldehyde* (0·40 g.) and cinnamamide (0·735 g.) were heated as usual for ten hours on water-bath. A hard solid came out with an orange tinge. After washing as above, a white crude product was obtained melting at 165–170°, with a change into an orange colour and a slight melting at 125–130° and resolidification. Recrystallised from methyl alcohol it came out quite white, but again developed on orange colour and a slight melting appearance at 135–137°, solidifying above 137° and finally melting completely at 181°. Repeated recrystallisations from methyl alcohol and from acetone failed to do away with this phenomena which continued. It weighed 0·80 g.

Cl, found 7·902%: chlorosalicylidene-*mono*cinnamamide $C_{16}H_{12}O_2NCl$ requires 12·44%, and chlorosalicylidene-*bis*cinnamamide $C_{25}H_{21}O_3N_2Cl$ requires 8·208%. The yield of the -*bis*compound was 72·36%.

Heating at 100–110° gave only a resinous mass. The compound was soluble in methyl alcohol, acetone and glacial acetic acid. It decolourised alkaline permanganate but did not give a pink colour with concentrated sulphuric acid.

3:5-*Dichlorosalicylaldehyde* (0·50 g.) and cinnamamide (0·735 g., 1:2 mol.) were heated on water-bath for ten hours; the homogeneous liquid which formed very soon solidified also quickly, in one hour. It had an orange yellow colour. Taken out as before, the white crude product melted at 200–204°: recrystallised from acetone, it finally melted at 205° and weighed 1·1 g.

Cl, found 15·23%; dichlorosalicylidene-*mono*cinnamamide $C_{16}H_{11}O_2NCl_2$ requires 22·19%, while dichlorosalicylidene-*bis*cinnamamide $C_{25}H_{20}O_3N_2Cl_2$ requires 15·20%. The yield was about 90%.

When the heating was at 100–110°, the yield was about quantitative. It had the same properties as those described above, except that it was soluble in acetone and in glacial acetic acid and was only sparingly soluble in methyl alcohol.

To the table on page 63[19] the following addition is made:—

Phenylacetamide	..	85·7 *mono*	57·46 *bis*	86·24	*bis*
Cinnamamide	..	Not done	72·36 „	Quantitative	„

Summary

Salicylaldehyde-amide condensations always produced the salicylidene-*mono*amides and the highest yield was always obtained in the presence of pyridine.[7] The 5-chlorosalicylaldehyde and the 3:5-dichlorosalicylaldehyde gave the best yield usually when heated alone; the product was almost always the *-bis* in the case of the latter, and generally so in the case of the former. The condensations with cinnamamide gave a quicker and a higher yield, it being quantitative in the case of the dichlorosalicylaldehyde. As before a temperature slightly higher than that of the water-bath produced generally a better yield in the last two amide condensations.

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STUDIES ON THE CHEMISTRY OF BORDEAUX MIXTURE—PART I

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(Communicated by Dr. B. Sanjiva Rao, F.A.SC.)

1. Introduction

The chemistry of Bordeaux mixture has been a controversial subject for the past 50 years. On adding copper sulphate to a suspension of calcium hydroxide in the proportion 5: 5: 50 (5 lbs. copper sulphate; 5 lbs. calcium oxide; 50 gallons water) to give alkaline Bordeaux mixture, a gelatinous greenish-blue precipitate is formed, which in the course of 2 to 4 hours turns to a compact deep blue solid. Several investigators have examined the composition of the deep blue product and have reported the solid to consist of various basic compounds such as (*a*) 10 CuO SO_3 4 CaO SO_3 [Pickering[7]], (*b*) 5 CuO SO_3 CaO; 5 CuO SO_3 2 CaO (Sicard[9]), (*c*) 5 CuO SO_3 [Wober,[12] Pratolongo and Allan[8]]. Martin[4] has put forward the view that Bordeaux mixture consists of cupric hydroxide which has been stabilised by adsorption of calcium sulphate. But Alessandro Baroni and Marini Betollo[1] report that cupric hydroxide was not found in any sample of Bordeaux mixture they examined by X-ray analysis. By an electrometric titration, Paul Mandain-Monval and Jean Bloy[5] have shown that cupric hydroxide is precipitated when copper sulphate solution is added to milk of lime in the concentration used for Bordeaux mixture.

The author of this paper is of opinion that the conflicting views found in literature regarding the composition of the Bordeaux solid are due to the colloidal nature of the system constituting Bordeaux mixture. Freshly prepared Bordeaux mixture contains cupric hydroxide in a gelatinous and hydrous condition and like most hydrous oxides, cupric hydroxide exhibits a marked tendency to adsorb other compounds from solution. Further, cupric hydroxide shows variations in its properties on " ageing ".

Apart from the deep blue solid, Bordeaux mixture (5: 5: 50) contains calcium hydroxide in excess and calcium sulphate formed during the reaction. Freshly formed cupric hydroxide has been found to take up considerable amounts of these calcium compounds from the aqueous phase to form the deep blue solid. The present investigation deals with a systematic study

of the reaction between copper sulphate and calcium hydroxide at various concentrations of calcium hydroxide and calcium sulphate in the aqueous phase with a view to decide whether the deep blue solid in Bordeaux mixture is an adsorption product. To confirm the results obtained with Bordeaux mixture, adsorption studies have also been carried out, starting with cupric hydroxide prepared by other reactions.

2. General Experimental Procedure

The greenish blue precipitate formed on adding copper sulphate to an excess of calcium hydroxide contains practically all the added copper in insoluble form, except a very small amount, which is in solution in the aqueous phase. In all the systems studied in this paper, the minute amounts of copper in solution in the aqueous phase were determined as these values were found to reveal the physical as well as the chemical changes undergone by the precipitate. All the systems showed an abrupt change in the concentration of copper in the aqueous phase whenever there was a change in the composition of the solid phase.

To determine the minute amount of copper in the aqueous phase, the systems had to be passed through a filter which, while not adsorbing any copper from the solution, completely retained the fine particles of the solid. Sintered Jena glass filters (1G3 and 1G4), quartz filter (No. 4), and Whatman filter-paper No. 50 (1·5 cm. disc held by ground glass tubes as in Schwinger's vacuum micro filter) were tested, using suitable automatic filtering device, with an arrangement to protect the solution from atmospheric carbon dioxide, ammonia, etc. All the filters used were found to adsorb copper from the solution during filtration, adsorption being particularly high with filter paper. Suitable quantities of filtrates had therefore to be rejected before collecting the samples for analysis. Samples obtained did not show any Tyndall effect, when examined in a powerful beam of light. As a result of these studies, Jena filter 1G4 with a filter disc of 3 cms. diameter, was found to be the most suitable.

Of the numerous microchemical methods available for the estimation of copper, the colorimetric method based on the use of sodium diethyldithio-carbamate, on suitable adaptation was found to be the most convenient [Callan and Henderson[2]; Moseley, *et al.*,[6] Mc Farlane[3]]. When the solution to be analysed contained a low concentration of copper ($< 0{\cdot}2$ mg. copper/litre), the yellow complex produced by the reagent with copper was extracted with amyl alcohol and the colour comparison of the extracts was made in a Hellige wedge colorimeter. With a copper content exceeding 0·2 mg. copper/litre, the yellow colour was developed in aqueous

solution in presence of gelatin (Mosely, *et al.*[6]) and colour comparison was made, without recourse to extraction, in double-plane 50 c.c. Nessler tubes. Standards for colour comparison were prepared from a dilute acidified copper sulphate solution containing 5 γ copper per c.c. Copper free water, prepared by redistilling distilled water in an all-glass Jena apparatus was used for all the experimental work.

The filtrates were also analysed for Ca^{++}, SO_4^{--} and OH^-. The calcium was estimated volumetrically by the oxalate method. 'Sulphate' was determined gravimetrically as barium sulphate. OH^- was determined by titrating with standard hydrochloric acid.

As the systems studied contained calcium hydroxide, the mixture had to be kept in Jena bottles, carefully protected against atmospheric carbon dioxide. All the measurements were made at the laboratory temperature (about 25° C.).

3. Experiments on the Composition of the Deep Blue Solid in Bordeaux Mixture

Influence of calcium sulphate and calcium hydroxide on the stability of cupric hydroxide.—According to Martin,[4] the precipitate formed by the action of excess of calcium hydroxide on copper sulphate consists of cupric hydroxide stabilised by adsorption of calcium sulphate.

It is well known that cupric hydroxide prepared the action of sodium hydroxide on a dilute solution of copper sulphate loses its characteristic blue colour rapidly. If calcium sulphate alone is sufficient to stabilise cupric hydroxide, it should be possible to obtain a blue product like the Bordeaux solid on treating cupric hydroxide with calcium sulphate. In order to test this view, a system containing cupric hydroxide in contact with saturated calcium sulphate only was prepared thus :—Dilute solutions of copper sulphate and limewater were mixed in equivalent proportions with efficient stirring and an excess of solid calcium sulphate ($CaSO_4.2H_2O$) was then added and the mixture agitated in a shaking machine for half an hour. The mixture was then filtered and the filtrate analysed for copper and calcium. The precipitate was then left in contact with a fresh sample of saturated calcium sulphate and refiltered. This treatment was repeated several times. The aqueous phase in each case was analysed for copper and calcium (Table I).

The results of the above experiment (Table I) show that cupric hydroxide is stable in presence of saturated calcium sulphate solution but the solid has a green colour, unlike the Bordeaux solid which is deep blue. Further, the copper in solution in this system is variable (from 0·63 to 0·035 mg.

TABLE I

Period of 'ageing' of precipitate in contact with saturated $CaSO_4$ solution (1)	Colour of precipitate (2)	Copper in solution mg./litre (3)	Calcium present as calcium sulphate mole per litre (4)
1 hour	Green	0·63	0·0156
24 hours	,,	0·41	0·0153
5 days	,,	0·135	0·0161
20 days	,,	0·035	0·0153
2 months	,,	0·27	..
4 months	,,	0·23	..

per litre) while in Bordeaux mixture the equilibrium value for copper in solution is practically constant at 0·47 to 0·54 mg. per litre. The system consisting of cupric hydroxide in contact with saturated calcium sulphate solution is evidently different from Bordeaux mixture, on account of the absence of calcium hydroxide. It is therefore significant to note that the green solid from this experiment gave a deep blue solid on treatment with a mixture of saturated calcium hydroxide and calcium sulphate and the blue solid had practically the same solubility—namely 0·56 mg. Cu per litre as the Bordeaux solid. This shows that calcium hydroxide is also necessary along with calcium sulphate to produce a system identical with Bordeaux mixture.

To investigate the role of calcium hydroxide, the behaviour of cupric hydroxide in saturated calcium hydroxide only (*i.e.*, in absence of calcium sulphate) was studied. Dilute solutions of copper sulphate (0·02 molar) and lime water (0·021 molar) were mixed in equivalent proportions in presence of a large volume of CO_2-free water, with efficient stirring. A greenish-blue precipitate was formed which held 25% of the original sulphate with it, as shown by the analysis of the aqueous phase. There was only a trace of alkali left over in the aqueous phase. The precipitate was washed repeatedly with about 500 c.c. of saturated calcium hydroxide each time, to remove the adsorbed calcium sulphate from it. When no more 'sulphate' was released to the solution, the solid was shaken repeatedly with fresh samples of saturated calcium hydroxide. The mixture was filtered after each treatment and the copper and calcium hydroxide in solution were determined (Table II).

In the above experiment, a greenish-blue precipitate was formed as usual on the addition of copper sulphate to lime water but the precipitate turned brown on washing it with calcium hydroxide, showing that in absence

TABLE II

Period of 'ageing' of precipitate (1)	Colour of precipitate (2)	Copper in solution mg. cu/litre (3)	$Ca(OH_2)$ in solution mole/litre (4)
3 hours	Greenish-blue	5·20	0·02202
24 hours	Brown	3·33	0·02210
1 month	Deep brown	0·42	0·02141
2 months	,,	0·33	0·02198
2½ months	,,	0·31	0·02187
4 months	,,	0·30	0·02169

of calcium sulphate the blue cupric hydroxide is unstable. The values for copper in solution show that the solubility of the precipitate decreases considerably on ' ageing ' and the equilibrium value (0·30 mg. copper per litre of solution) is far different from that of Bordeaux mixture. Finally, the brown solid was treated with a mixture of calcium hydroxide and calcium sulphate in excess but the solid remained unchanged in colour and the copper in solution was only 0·24 mg. copper per litre of solution, as against 0·47 to 0·54 mg. Cu per litre in Bordeaux mixture. This shows that the brown cupric hydroxide cannot be transformed to the deep blue solid even on prolonged contact (2 months) with excess of calcium hydroxide and calcium sulphate.

In the above experiment, the cupric hydroxide was rendered free from adsorbed calcium sulphate by repeatedly washing it with saturated calcium hydroxide but the removal of calcium sulphate was slow. To eliminate the calcium sulphate from the system completely, the cupric hydroxide was prepared by mixing equivalent amounts of copper sulphate and barium hydroxide in presence of calcium hydroxide suspended in water. The resulting system consisting of $Cu(OH)_2 + BaSO_4 + Ca(OH)_2$ (solid phase) in saturated calcium hydroxide solution was filtered at intervals and copper in the filtrate was determined (System A, Table III). A part of the same mixture was treated, immediately after its preparation, with a mixture of calcium hydroxide and calcium sulphate in excess and the copper in the aqueous phase was determined (System B, Table III).

In system A containing only calcium hydroxide in aqueous phase, the precipitate of cupric hydroxide formed was greenish-blue at 4 hours from the commencement of the experiment and became deep blue with a violet shade after about 24 hours. Thereafter, the precipitate remained violet-blue till 7 days, after which it showed signs of blackening and became brownish-violet and finally brown. The results for copper in solution in this system (column 3, Table III) show that the violet-blue solid has a high

TABLE III

Ageing of precipitate	System A Solid phase :— $Cu(OH)_2+BaSO_4+Ca(OH)_2$ Aq. phase :— $Ca(OH)_2$		System B Solid phase :— $Cu(OH)_2+BaSO_4+Ca(OH)_2+CaSO_4$ Aq. phase :— $Ca(OH)_2+CaSO_4$	
(1)	Colour of precipitate (2)	Copper in solution in mg. Cu/litre (3)	Colour of precipitate (4)	Copper in solution mg. Cu/litre (5)
9 hours ..	Greenish-blue	4·5	Greenish-blue	1·22
24 hours ..	Blue with violet shade	1·78	Deep-blue	0·56
3 days ..	Violet-blue	1·62	Deep-blue	0·58
9 days ..	Brownish-violet	1·64	do	0·53
2 months ..	Brown	0·40	do	0·54

solubility with respect to copper and the solubility is almost constant for a period of 8 days (1·78, 1·62, 1·64 mg. Cu per litre). The brown solid resulting from it has a low solubility of 0·4 mg. copper per litre in the same aqueous medium. This sudden decrease in solubility from 1·64 to 0·40 mg. Cu per litre and the change in the colour of the solid from bluish-violet to brown show that there is a change in composition of the solid phase after 9 days.

In System B containing calcium hydroxide and calcium sulphate in the solid and the aqueous phases, the precipitate became deep blue like the Bordeaux solid in the course of 4 hours after its preparation and remained unchanged in colour throughout. The equilibrium value for copper in solution in this system was the same as that of Bordeaux mixture, *i.e.*, 0·54 mg. Cu per litre.

These experiments show that in the total absence of calcium sulphate the blue precipitate of cupric hydroxide undergoes dehydration to the brown variety. Further, freshly precipitated cupric hydroxide on treatment with a mixture of saturated calcium hydroxide and calcium sulphate gives a system practically identical with Bordeaux mixture.

4. Adsorption of Calcium Hydroxide and Calcium Sulphate by Cupric Hydroxide

The experiments described in Section 3 of this paper show that both calcium hydroxide and calcium sulphate have profound influence in transforming cupric hydroxide to a stable blue product. Preliminary experiments

showed that cupric hydroxide took up large quantities of these calcium compounds from solution during its transformation to the deep blue form. The maximum amounts of these calcium compounds taken up by cupric hydroxide were therefore determined. The extent of adsorption could conveniently be determined by shaking till the attainment of equilibrium, 0·01 mole of cupric hydroxide (prepared by addition of copper sulphate to lime water in excess) repeatedly with suitable amounts of an analysed mixture of saturated calcium hydroxide and calcium sulphate solution (carefully freed from the solid compounds). The decrease in concentration of calcium hydroxide and calcium sulphate in the aqueous phase was determined by analysis (Table IV).

TABLE IV

No. of Experiment	$Ca(OH)_2$ adsorbed in mole per mole $Cu(OH)_2$	$CaSO_4$ adsorbed in mole per mole $Cu(OH)_2$	Copper in aqueous phase in the system at equilibrium: in mg. Cu per litre
1	0·774	0·264	0·52
2	0·743	0·243	0·50

The above adsorption measurements were also carried out with a sample of cupric hydroxide prepared by action of sodium hydroxide on copper sulphate (Weiser, *et. al.*[11]). This cupric hydroxide was treated repeatedly with an analysed mixture of saturated calcium hydroxide and calcium sulphate and the aqueous phase was filtered off and analysed. Finally the solid product was also analysed for the calcium compounds contained in it. The results of this experiment are given in Table V.

Amount of $Cu(OH)_2$ taken	$Ca(OH)_2$ adsorbed in mole per mole $Cu(OH)_2$		$CaSO_4$ adsorbed in mole per mole $Cu(OH)_2$		Copper in soln. the system at equilibrium mg. Cu per litre
	By analysis of aqueous phase	By analysis of blue solid	By analysis of aq. phase	By analysis of the blue solid	
0·005 mole	0·855	0·885	0·250	0·262	0·24

In all the above adsorption experiments, a compact deep blue product exactly similar to the Bordeaux solid was finally obtained but its solubility with respect to copper in the mixture of saturated $Ca(OH)_2$ and $CaSO_4$ was not the same as that of the Bordeaux solid except in experiments 1 and 2. The total amounts of $Ca(OH)_2$ and $CaSO_4$ taken up per mole $Cu(OH)_2$ are somewhat higher in the case of the sample prepared by the action of

TABLE VI

1	2	3	4	5	6	7	
No. of Experiment	Amount of $Cu(OH)_2$ in mole	Period of 'ageing' of ppt.	Colour of the sample	Copper in solution Cu in mg. per litre	$CaSO_4$ in aqueous phase mole per litre $\times 10^3$	$CaSO_4$ adsorbed in mole/mole $Cu(OH)_2$	
						By analysis of aqueous phase	By analysis of the solid
1	0·02	1 months	deep-blue*	0·65	9·42	0·295	
		3 months	do	0·64	9·30	do	..
2	0·02	1 month	deep-blue*	0·65	7·16	0·296	
		3 months	do	0·67	6·96	do	..
3	0·02	1 month	deep-blue*	0·69	4·75	0·313	
		3 months	do	0·71	4·70	do	..
4	0·025	2 hours	Greenish-blue	3·60	3·86	0·228	
		24 hours	Deep-blue*	0·89	3·68	0·260	
		5 days	do	0·75	do	do	
		1 month	do	0·74	3·65	do	0·250
5	0·016	1 hour	Greenish-blue	4·06	3·02	0·293	
		5 days	Deep-blue*	0·86	3·00	0·293	
		1 month	Deep blue	0·84	2·92	0·306	
		2 months	do	0·83	2·98	do	..
6	0·01	2 hours	Greenish-blue	3·03	1·63	0·185	
		5 days	Deep-blue	1·78	1·52	0·231	
		1½ months	do	0·69	1·47	0·251	
		3 months	do	0·65	1·43	0·264	
		6 months	do	0·62	1·43	do	0·252
7	0·005	2 hours	Greenish-blue	3·85	0·82	0·178	
		5 days	Light-blue	2·24	0·85	0·157	
		30 days	do	2·14	0·85	do	
		1½ months	Deep-blue	..	..	..	
		3 months	do with slight dark shade	0·94	0·65	0·235	
		6 months	Bluish-grey	0·80	0·65	do	0·231
8	0·00375	2 hours	Greenish-blue	3·78	0·62	0·172	
		15 days	Light-blue	2·29	0·63	0·160	
		1 month	Brown	..	..	..	
		2 months	do	0·83	0·83	0·021	
		3 months	do	0·41	0·83	0·021	0·016
9	0·0025	3 hours	Green with blue shade	3·43	0·42	0·152	
		5 days	Light-blue	2·59	0·42	do	
		16 days	Light-blue with brown shade	2·33	0·43	0·144	
		1 month	Brown	0·57	0·88	0·026	
		2 months	do	0·39	0·83	0·026	0·018

* In these experiments, a greenish-blue precipitate is formed by the reaction and the precipitate becomes deep blue in about 3 hours after precipitation.

sodium hydroxide on copper sulphate (Table V) but are not far different from the results got in the first two experiments in which $Cu(OH)_2$ prepared by the action of copper sulphate on calcium hydroxide was employed.

5. Effect of Concentration of Calcium Hydroxide and Calcium Sulphate on the Stability of Cupric Hydroxide

In the experiments described in this section, an attempt has been made to determine the relationship between the stability of cupric hydroxide and the concentration of calcium hydroxide and calcium sulphate in the aqueous phase in contact with it. The general procedure employed in this study has been to vary the concentration of one of these calcium compounds at a time, keeping the concentration of the other, constant at its saturation value. The extent of adsorption of the calcium compound whose concentration is varied, has been determined.

Table VI contains experimental results showing the extent of adsorption of calcium sulphate by cupric hydroxide from solutions containing varying concentrations of calcium sulphate but saturated with respect to calcium hydroxide. The cupric hydroxide was precipitated by adding known amount of copper sulphate to calcium hydroxide in excess, suspended in a suitable quantity of water and the amount of calcium sulphate adsorbed was determined by estimating the sulphate in the aqueous phase as well as in the solid product at the end of the experiment. A blank experiment showed that the adsorption of calcium sulphate by solid calcium hydroxide present in excess in these systems was negligibly small.

The following conclusions may be drawn from the experimental results in Table VI.

1. The cupric hydroxide adsorbs practically a constant amount of calcium sulphate [0·25 mole per mole $Cu(OH)_2$], when the concentration of calcium sulphate in the aqueous phase is above $1{\cdot}63 \times 10^{-3}$ mole per litre (experiments 1 to 6). Most of this adsorbed calcium sulphate is taken up during the precipitation of cupric hydroxide (Expts. 4 & 5). The precipitate becomes deep blue in about 3 hours and retains the blue colour for a long period.

2. At concentrations of calcium sulphate below $1{\cdot}63 \times 10^{-3}$ mole per litre of solution, the cupric hydroxide loses its stability, owing to inadequate adsorption of calcium sulphate. The precipitate changes over to the blue form after a long period and finally undergoes decomposition to a brown solid losing practically all the adsorbed calcium sulphate (Experiments 8 & 9). The stability of cupric hydroxide is therefore dependent on the presence of a minimum concentration of calcium sulphate

($1 \cdot 63 \times 10^{-3}$ mole $CaSO_4$ per litre) in the aqueous phase, saturated with calcium hydroxide.

6. Adsorption of Calcium Hydroxide by Cupric Hydroxide at Different Concentrations of the Former

In Section 4 of this paper, it has been shown that cupric hydroxide takes up nearly 0·75 mole of calcium hydroxide from a saturated mixture of calcium hydroxide and calcium sulphate solution. In view of the large amount of calcium hydroxide taken up, it becomes very important to determine whether the amount of $Ca(OH)_2$ adsorbed varies with the concentration of $Ca(OH)_2$ in the aqueous phase. Experiments in this direction are now in progress. The results so far obtained seem to indicate that a small amount of calcium hydroxide is initially adsorbed during the precipitation of cupric hydroxide by action of copper sulphate on lime water and the amount so adsorbed varies with the concentration of calcium hydroxide left over in the aqueous phase. On increasing the concentration of calcium hydroxide up to a limiting value, keeping the concentration of calcium sulphate constant, a further amount of calcium hydroxide is taken up *abruptly* by the cupric hydroxide. The author hopes to complete this work shortly and publish the results.

7. Desorption of the Adsorbed Calcium Hydroxide and Calcium Sulphate

The possibility of removing the adsorbed $Ca(OH)_2$ and $CaSO_4$ from the deep blue solid has been investigated to see whether the calcium compounds are held loosely by the solid and whether the processes of adsorption and desorption are reversible. Martin[4] has shown that the deep blue Bordeaux solid turns black when repeatedly washed with water. The desorption experiments described in this section of the paper show that the decomposition of Bordeaux solid to the black cupric oxide is undoubtedly due to the removal of the calcium compounds associated with it. However, the deep blue solid from the 5: 5: 50 Bordeaux mixture is not suitable for the quantitative study of desorption, as it contains excess of solid $Ca(OH)_2$ and $CaSO_4\ 2H_2O$ mixed up with it. Therefore the deep blue solid from one of the adsorption experiments (Expt. 2, Table IV) which was in equilibrium with a mixture of saturated calcium hydroxide and calcium sulphate solution but free from the solids, was selected for the purpose and was shaken up repeatedly with small portions of saturated calcium sulphate solution, to bring about the desorption af calcium hydroxide from the solid. The clear liquid was decanted into a bottle. The decanted liquid was finally filtered and a suitable volume of the filtrate was titrated against 0·1 N hydrochloric acid. The

treatment of the solid with saturated calcium sulphate was repeated till no more calcium hydroxide was extracted. 0·59 mole out of 0·743 mole of adsorbed $Ca(OH)_2$ [per mole $Cu(OH)_2$] was extracted in this manner, but desorption was very slow from the beginning. The desorption of the remaining 0·153 mole (about 20% of the total amount adsorbed) of the calcium hydroxide per mole $Cu(OH)_2$ became very difficult in practice and the experiment was given up. However during this desorption of calcium hydroxide, the solid did not lose any adsorbed calcium sulphate as was shown by the determination of sulphate in the solution got by the extraction. The deep blue colour of the solid during this treatment became gradually bluish-green and finally green, confirming the result already referred to—namely, that the adsorbed calcium hydroxide is primarily responsible for the formation of the *deep blue* solid. This experiment shows that most of adsorbed calcium hydroxide except a small portion which is held tenaciously can be removed from the cupric hydroxide by the simple process of washing with calcium sulphate.

It is also necessary to investigate whether desorption of calcium hydroxide will occur when the concentration of calcium hydroxide is progressively decreased. An experiment in this direction is now in progress.

A similar experiment on the stepwise desorption of calcium sulphate from the stabilised cupric hydroxide has been carried out in this manner : 0·02 mole of cupric hydroxide prepared by adding copper sulphate to lime water was repeatedly treated with a fresh mixture of saturated calcium hydroxide and calcium sulphate solution till equilibrium was reached. The desorption of calcium sulphate from the deep blue product was then studied, by decreasing the concentration of calcium sulphate in the aqueous phase, in a stepwise manner, keeping the solution saturated with calcium hydroxide. The blue solid was treated successively with 10 solutions (over a total period of several months) in which the concentration of calcium sulphate was progressively decreased from 0·012 mole per litre to zero value, keeping each solution in contact with the solid for about 10 days. The analyses of these solutions before and after treatment with the solid showed that there was no desorption of calcium sulphate, even when the solid was in contact with a low concentration of calcium sulphate, *i.e.*, $0{\cdot}165 \times 10^{-3}$ mole $CaSO_4$ per litre of solution. When, however, the solid was treated with merely saturated calcium hydroxide solution, the desorption of calcium sulphate occurred slowly and the blue solid changed over to brown variety. Even the brown solid was found to lose the calcium sulphate slowly as only 10% of the absorbed calcium sulphate was released to the lime water in about months. This experiment shows that the desorption of calcium sulphate

is a slow process and the adsorption and desorption processes are not reversible.

Summary

1. Freshly prepared Bordeaux mixture (5: 5: 50) consists of a gelatinous greenish-blue precipitate of cupric hydroxide which turns to a compact deep blue solid in 2 to 4 hours after preparation.

2. The stability of the deep blue solid depends upon the presence of both calcium hydroxide and calcium sulphate in the aqueous phase. Freshly precipitated cupric hydroxide will become green in saturated calcium sulphate solution, brown in saturated calcium hydroxide and deep blue in a mixture of saturated calcium hydroxide and calcium sulphate. The copper in aqueous phase in the last system will be practically the same as in 5: 5: 50 Bordeaux mixture (*i.e.*, 0·54 mg. Cu/litre) while in the other two systems it will be far different.

3. Freshly precipitated cupric hydroxide takes up 0·75 mole calcium hydroxide and 0·25 mole calcium sulphate per mole cupric hydroxide, from a saturated solution containing both the calcium compounds, giving a deep blue product practically identical with the blue solid in Bordeaux mixture.

4. The adsorption of these calcium compounds by cupric hydroxide at different concentrations of them in the aqueous phase has been studied to find out whether the blue solid is an adsorption complex. In presence of excess calcium hydroxide, cupric hydroxide takes up practically a constant amount of calcium sulphate, *i.e.*, 0·25 mole per mole cupric hydroxide whenever the concentration of calcium sulphate produced in the aqueous phase exceeds a limiting value, namely $1 \cdot 63 \times 10^{-3}$ mole $CaSO_4$/litre. At lower concentrations of calcium sulphate, the cupric hydroxide undergoes decomposition to brown hydrous cupric oxide, with loss of the adsorbed calcium sulphate.

5. The desorption of each of the calcium compounds from the blue solid has been studied by decreasing the concentration of the calcium compounds, one at a time, in the aqueous phase. The desorption of calcium sulphate occurs slowly when the blue solid is treated with saturated calcium hydroxide solution and the sample undergoes decomposition to a brown solid. The blue solid turns green with loss of about 80% of calcium hydroxide held by it on washing the sample repeatedly with saturated calcium sulphate solution. The adsorption and desorption processes are not reversible.

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